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INTERFERENCES MECHANISMS IN WASTE STABILIZATION/SOLIDIFICATION PROCESSES

by

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16. ABSTRACT

The stabilization/solidification of hazardous wastes involves a series of chemical treatment procedures. The waste is normally treated so as to complex or bind the contaminants into a stable, insoluble form (stabilization), or to entrap the waste material in a solid and/or crystalline matrix (solidification). Hazardous wastes contain many constituents that could interfere with the binding process. This project is concerned with identifying possible interference mechanisms between particular waste components and commercially available waste-binding systems.

This report presents a literature review and information concerning Portland cement and pozzolan chemistry, the effects of added constituents (admixtures) on their setting characteristics, and the effects of typical organic waste components on the physical and containment properties of the treated waste product. These topics are presented so that conclusions may be drawn as to possible types of interference materials that might be encountered in typical waste/binder systems. Also included are a glossary of common cement terminology and three bibliographic appendices covering a compilation of references and annotated citations for both Portland cement and asphaltic waste treatment systems.

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FOREWORD

Today's rapidly developing and changing technologies and industrial products and practices frequently carry with them the increased generation of materials that, if improperly dealt with, can threaten both public health and the environment. The U.S. Environmental Protection Agency is charged by Congress with protecting the Nation's land, air, and water resources. Under a mandate of national environmental laws, the Agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. These laws direct the EPA to perform research to define our environmental problems, measure the impacts, and search for solutions.

The Risk Reduction Engineering Laboratory is responsible for planning, implementing, and managing research, development, and demonstration programs to provide an authoritative, defensible engineering basis in support of the policies, programs, and regulations of the EPA with respect to drinking water, wastewater, pesticides, toxic substances, solid and hazardous wastes, and Superfund-related activities. This publication is one of the products of that research and provides a vital communication link between the researcher and the user community.

This report reviews the literature concerning the possible effects of waste constituents on the long-term durability and waste containment characteristics of waste stabilized/solidified using the most common binder systems: cement, pozzolan, and asphalt. This information should be of assistance to planners and engineers who are designing and specifying waste treatment systems. The goal is to provide the background necessary for a state-of-the-art understanding of the benefits and limitations of stabilization/solidification processes.

E. Timothy Oppelt, Acting Director
Risk Reduction Engineering Laboratory

ABSTRACT

The stabilization/solidification of hazardous wastes involves a series of chemical treatment procedures. The waste is normally treated so as to complex or bind the contaminants into a stable, insoluble form (stabilization), or to entrap the waste material in a solid and/or crystalline matrix (solidification). Hazardous wastes contain many constituents that could interfere with the binding process. This project is concerned with identifying possible interference mechanisms between particular waste components and commercially available waste-binding systems.

This report presents a literature review and information concerning Portland cement and pozzolan chemistry, the effects of added constituents (admixtures) on their setting characteristics, and the effects of typical organic waste components on the physical and containment properties of the treated waste product. These topics are presented so that conclusions may be drawn as to possible types of interference materials that might be encountered in typical waste/binder systems. Also included are a glossary of common cement terminology and three bibliographic appendices covering a compilation of references and annotated citations for both Portland cement and asphaltic waste treatment systems.

NOTICE

The information in this document has been funded wholly or in part by the United States Environmental Protection Agency under Interagency Agreement No. DW219306080-01-0 to the U.S. Army Engineer Waterways Experiment Station. It has been subjected to the Agency's peer and administrative review, and it has been approved for publication as an EPA document. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

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The study was conducted under the general supervision of Dr. John Harrison, Chief, EL; Dr. Raymond L. Montgomery, Chief, Environmental Engineering Division; and Mr. Norman R. Francingues, Jr., Chief, Water Supply and Waste Treatment Group. Commander and Director of WES was COL Dwayne G. Lee, CE; Technical Director was Dr. Robert W. Whalin.

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SECTION 1

INTRODUCTION

Waste treatment processes that are designed to decrease the toxicity or volume of hazardous wastes (e.g., precipitation or incineration) generate persistent residues that must be prepared for safe final or ultimate disposal. In most cases, final disposal of these residuals is by means of secure, shallow-land burial. The disposal problem is most critical in the case of wastes that cannot be destroyed or detoxified, such as heavy metal sludges and brines. Thus, even with improved waste treatment methods, there will continue to be a need for technology related to the safe land disposal of hazardous wastes. Stabilization/solidification (S/S) of hazardous wastes before final disposal has been proposed as a way to prevent release of the hazardous waste constituents to the environment.

According to Title 40 of the Code of Federal Regulations, the U.S. Environmental Protection Agency is responsible for evaluating the suitability of hazardous waste for land disposal and for the examination of hazardous waste delisting petitions. A thorough understanding of the potential behavior of stabilized/solidified wastes is necessary to make judgments as to the long-term effectiveness of their containment. The extent to which various contaminants are securely held in stabilized/solidified wastes must be determined for all S/S processes so that individual processes and delisting petitions can be evaluated. There are several available methods for the S/S of hazardous wastes. These methods have been developed primarily for inorganic wastes. However, organic wastes are increasingly being included as their volume continues to increase and S/S additives and technology improve. Some of the chemical components of the complex wastes may interfere with the proposed S/S process and cause undesired results (e.g., flash set, set retardation, spalling, etc.). This report surveys the literature concerned with the effects of various waste constituents on the most common S/S binder systems: Portland cement, pozzolan, and asphalt. At this time there is a paucity of quantitative data concerning the specific effects of these interfering compounds alone or in concert upon particular S/S processes.

LITERATURE SEARCH PROCEDURES

The literature search was conducted using facilities available in the U.S. Army Engineer Waterways Experiment Station (WES) Library and the WES Concrete Technology Division Library. The search included American Cement Institute Journals and Indexes, American Society for Testing and Materials (ASTM) Journals and Indexes, "Cement and Concrete Research" Journals, "Chemical Abstracts," available textbooks, personal libraries and files of the Concrete Technology Division staff members, and telephone communication with various experts in the field of S/S of hazardous wastes.

The Technical Information Center at the WES conducted two computer searches using the Compendex Data Base, National Technology Information

Service Data Base, and Technical Research Information Service Data Base using the following key words:

- additives
- admixture
- asphalt
- asphaltic cement
- chemical
- chemical solidification
- interference
- organic
- organic waste
- Portland cement
- set time
- solidification
- solidify
- stabilization
- stabilize
- waste

Additional computer searches were conducted using the Data Base Index (DBI), Chemical Abstracts Data Base, Engineering Information and Technical Meetings Data Base (EIMET), Environment Abstracts Data Base (ENVIROLINE), Electrical Power Information Abstracts Data Base (EPIA), and Geological References Data Base (GEOREF) of the American Geological Institute. The following key words were used:

- admixtures
- cement
- chemical interference
- hazardous waste
- interference
- Portland cement
- solidification
- stabilization

Three bibliographies developed through these procedures are included as appendices. Appendix A is an annotated bibliography of references on effects of additives on Portland cement concrete, listed alphabetically by first key word in the title. Appendix B is an annotated bibliography of references on the effects of additives on asphalt materials, arranged similarly to Appendix A. Appendix C is an alphabetical listing of all applicable references, by author's name.

A glossary of cement chemistry terminology is presented as Appendix D.

EFFECTS OF SPECIFIC MATERIALS ON CEMENT AND POZZOLAN CHEMISTRY

Although chemical stabilization and solidification of hazardous wastes before disposal is increasing in importance, very little work has been done concerning the effects of specific waste components on the physical and containment properties of the final S/S waste product. Many categories of inorganic and organic materials are known to have either beneficial or harmful effects on concrete and asphalt products as used in the construction industry. Such admixtures (materials added to change the physical properties of concrete) are routinely added to concrete formulations to retard set, lower heat production, increase water resistance, and/or increase final product strength. Likewise, care has to be taken to see that aggregates or other components do not contain deleterious materials.

A review of cement literature reveals that the chemistry of the hardening of concrete is not well understood although the basic chemical reactions and their products are fairly well known. Several theories have been proposed and are discussed concerning how additives produce their effects by interfering with cement hydration reactions, but none appears to be entirely satisfactory.

Pozzolan chemistry is less well known, although it is thought to be analogous in some ways to that of Portland cement.

The complexity of the hydration reactions and the effects of slight variations in process formulations or mixing parameters complicate the prediction of the effects of additives on the final S/S waste product. Effects of single-component additions are only poorly understood. Predicting the effects of complex and variable compositions such as those found in a real waste is beyond the current state-of-the-art.

As an example, the use of short-term or accelerated curing tests for compressive strength may give erroneous results as to the long-term stability of the binder-waste mix. Materials that cause the retardation of set often bring about increased long-term strength in both Portland cement and lime/fly ash S/S systems. For mixes containing organic wastes or other known set retarders, a 90-day cure (in addition to 28-day samples) is recommended. This long curing time brings about obvious difficulties in the day-to-day operation of a waste S/S plant. No short-term testing protocols have yet been developed to adequately predict long-term stability, durability, and strength characteristics of S/S waste products.

Nonpolar organic materials of low volatility should not hinder strength development in cement or pozzolan systems. Since chlorinated hydrocarbons comprise a large proportion of the hazardous organic wastes, a study of their effects upon these systems is strongly recommended. Organic wastes that contain hydroxyl (e.g., sugars and alcohols) or carboxylic acid (e.g., citric acid, acetic acid) groups (and perhaps amines) can be expected to delay or stop altogether the pozzolanic reactions. These functional groups are present in wastes such as biological sludges, paint sludges, and many solvents.

The final properties of a waste-cement mixture are highly dependent upon: 1) the constituents of the waste that may interfere with the setting reactions; 2) the water/cement ratio which is the primary determinant of the size configuration of the void space and permeability of the final product; 3) presence of admixtures such as fly ash, surfactants, or others that may modify setting or final strength parameters of the product; and 4) procedures and conditions used for mixing and curing the treated wastes. The strength and durability of concrete products are directly related to the type and number of voids in the final product. Adequate design of the formulation and mixing parameters can change the durability and accessibility of water to waste constituents of the final S/S product by several orders of magnitude.

Asphaltic and polymeric materials used for waste S/S also are affected by low levels of some waste components. Solvents and oils may weaken and liquefy the asphaltic base. Oxidizers and some inorganic materials may cause or promote fires or flash-set of the final mixture. Care should be taken to thoroughly test specific wastes that are candidates for this treatment process.

STUDIES OF WASTE INTERFERENCE WITH S/S PROCESSES

A great variety in the types of reagents used and testing performed is found in the few published studies which allude to the effects of waste components on the S/S process. Details of materials and reagents, preparation and mixing procedures, and product testing protocols are often sketchy and incomplete. In this review, all reports which impinge upon effects of different waste constituents on specific S/S processes are discussed in the light of current testing and disposal requirements. No broad generalizations could be gleaned from the studies reviewed, but a list of those materials which should be studied further include heavy metals interferences such as lead, copper, and zinc; organics, such as grease and oils, phenolics, degreasers, and pesticides; and stringent conditions such as high sulfate and strong bases.

There is a clear need for further experimental work to obtain physical and chemical data relative to cementitious and asphaltic S/S treatment systems. Enough basic information should be developed so that valid prediction and modeling of waste-binder interactions are possible. This ability would overcome the current need to test each specific waste-binder combination for possible interferences. However, the variability and complexity of most waste streams, as well as cement and pozzolanic setting reactions, still may preclude broad generalizations.

SECTION 2

CONCLUSIONS AND RECOMMENDATIONS

Although chemical stabilization and solidification (S/S) of hazardous wastes before disposal is increasing in importance, very little work has been done concerning the effects of specific waste components on the physical and containment properties of the final S/S waste product. Many categories of inorganic and organic materials are known to have either beneficial or harmful effects on concrete and asphalt products as used in the construction industry. Such admixtures (materials added to change the physical properties of concrete) are routinely added to concrete formulations to retard set, lower heat production, increase water resistance, and/or increase final product strength. Likewise, care has to be taken to see that aggregates or other components do not contain deleterious materials.

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The final properties of waste-cement mixture are highly dependent upon: 1) the constituents of the waste that may interfere with the setting reactions; 2) the water/cement ratio, which is the primary determinant of the size and configuration of the void space and permeability of the final product; 3) presence of admixtures such as fly ash, surfactants, or others that may modify setting or final strength parameters of the product; and 4) procedures and conditions used for mixing and curing the treated wastes. The strength and durability of concrete products is directly related to the type and number of voids in the final product. Adequate design of the formulation and mixing parameters can change the durability and accessibility of water to waste constituents of the final S/S product by several orders of magnitude.

Asphaltic and polymeric materials used for waste S/S also are affected by low levels of some waste components. Solvents and oils may weaken and liquefy the asphaltic base. Oxidizers and some inorganic materials may cause or promote fires or flash set of the final mixture. Care should be taken to thoroughly test specific wastes that are candidates for this treatment process.

A great variety in the types of reagents used and the testing performed is found in the few published studies which allude to the effects of waste components on the S/S process. Details of materials and reagents, preparation and mixing procedures, and product testing protocols are often sketchy and incomplete. In this review, all reports that impinge upon the effects of different waste constituents on specific S/S processes are discussed in light of current testing and disposal requirements. No broad generalizations could be gleaned from the studies reviewed, but a list of those materials which appear to be appropriate for further study include heavy metals interferences, such as lead, copper and zinc; organics, such as grease and oils, phenolics, degreasers, and pesticides; and stringent conditions such as high sulfate and strong bases.

There is a clear need for further experimental work to obtain physical and chemical data relative to cementitious and asphaltic S/S treatment systems. Enough basic information should be developed using standard mixing and testing protocols so that valid prediction and modeling of waste-binder interactions are possible. The ability to generalize concerning interference effects would overcome the current need to test each specific waste-binder combination for possible interferences. However, the variability and complexity of most waste streams as well as cement and pozzolanic setting reactions may still preclude such generalizations.

SECTION 3

CEMENT AND POZZOLAN PROPERTIES THAT MAY AFFECT WASTE CONTAINMENT

INTRODUCTION

The ability of a stabilized/solidified (S/S) waste product to contain a given hazardous constituent depends primarily upon its resistance to leaching or volatilization of waste constituents and its long-term durability. This section develops the background necessary for an understanding of factors controlling leaching and durability characteristics of cement and pozzolanic systems.

Comparison of the finished S/S waste product with standard construction materials is not entirely appropriate since most hazardous wastes treated by S/S technologies are liquid slurries with relatively low solids content (10 to 40 percent solids by weight). The mixture of a solidification agent such as cement with a slurried waste more closely resembles a hydrated cement paste rather than a typical concrete with a large proportion of aggregate (60 to 80 percent of the final concrete volume). Experimentation with hydrated cement pastes provides a basis for speculation on the effects of various hazardous waste constituents on a S/S waste product.

As noted above, the characteristics of S/S wastes that are most important to waste containment are leachability and durability. However, unconfined compressive strength (UCS) is the commonly specified measure of concrete quality since it is determined easily and inexpensively by a reproducible test. No correlation has been demonstrated between UCS and leachability.

Coté et al. (1984) has based a theoretical model of the leaching of specific, low-to-high solubility material from a solid matrix to a large extent on the rate of internal diffusion of the material in the solid matrix. Internal diffusion of soluble ions or molecules in a solid matrix depends largely upon the relative amount and character of void spaces in the solid, which in turn relates directly to the permeability of the porous solid and its ultimate strength.

Numerous researchers have investigated the chemistry and the physical characteristics of cement and pozzolanic mixtures. These studies serve as an excellent foundation for understanding the similar properties of cement- and pozzolan-based S/S processes. This section presents a brief overview of cement and pozzolan chemistry and terminology. Detailed information on the subject is available in the following primary sources.

1. Bye, G. C. 1983. Portland Cement: Composition, Production and Properties. Pergamon Press, New York. 149 pp.

2. Mehta, P. K. 1987. Concrete Structure, Properties and Materials. Prentice-Hall, Inc., Englewood Cliffs, NJ.

3. Neville, A. M. 1981. Properties of Concrete. Pitman Publishing, Inc., Marshfield, MA.

4. Portland Cement Association. 1968. Design and Control of Concrete Mixtures. 11th ed., Portland Cement Association, Skokie, IL.

5. Powers, T. C. 1958. The Physical Structure and Engineering Properties of Concrete. Bulletin 90, Portland Cement Association, Skokie, IL.

6. U.S. Bureau of Reclamation. 1975. Concrete Manual. Washington, DC.

7. Woods, H. 1968. Durability of Concrete. ACI Monograph 4. American Concrete Institute, Detroit, MI.

PORTLAND CEMENT

Portland cement is probably the most common cementitious additive for the S/S of hazardous waste. Portland cement is highly uniform, relatively inexpensive, and widely available; it can be worked in normal construction machinery by unskilled labor; and it produces products with highly predictable characteristics. A variety of standard types of Portland cement are available for specific applications, and many admixtures have been developed to modify its setting and final properties.

The Solids in Hydrated Cement

The hydration of Portland cement is a series of simultaneous and consecutive reactions between water and solid cement constituents which occur in the setting and hardening processes. Anhydrous Portland cement consists of angular particles (usually 1 to 50 μm) with a chemical composition of the primary clinker materials that corresponds approximately to C_3S, C_2S, C_3A, and C_4AF, where $C = CaO$, $S = SiO_2$, $A = Al_2O_3$, $F = Fe_2O_3$, $\bar{S} = SO_3$, and $H = H_2O$. In ordinary Portland cements, the respective amounts range between 45 and 60, 15 and 30, 6 and 12, and 6 and 8 percent (with a small added amount of $C\bar{S}$). Table 1 lists selected characteristics of these materials.

Dispersing Portland cement in water causes the various constituents to go into solution, which rapidly saturates the liquid phase with the various ionic species. The first needle-like crystals of calcium sulfoaluminate hydrate (ettringite) appear within a few minutes of cement hydration (see Equation 2 below). After a few hours, large, prismatic crystals of calcium hydroxide (CH) and very small fibrous crystals of calcium silicate hydrates (C-S-H) begin to fill the empty spaces formerly occupied by water and the dissolving cement particles. The most important reactions in later stages are the hydration of calcium silicates (to produce C-S-H), which continues for many months at decreasing rates (Topovics 1979).

The rapid changes in the solution composition which occur upon initial hydration are followed by a relatively constant composition, depending upon the initial cement material and the water/cement ratio. The solution is

TABLE 1. PRINCIPAL COMPOUNDS OF PORTLAND CEMENT AND THEIR CHARACTERISTICS

Approximate composition	$3CaO \cdot SiO_2$	$\beta 2CaO \cdot SiO_2$	$3CaO \cdot Al_2O_3$	$4CaO \cdot Al_2O_3Fe_2O_3$
Abbreviated formula	C_3S	βC_2S	C_3A	C_4AF
Common name	Alite	Belite	---	Ferrite phase, Fss
Principal impurities	MgO, Al_2O_3, Fe_2O_3	MgO, Al_2O_3, Fe_2O_3	SiO_2, MgO, alkalies	SiO_2, MgO
Common crystalline form	Monoclinic	Monoclinic	Cubic, orthorhombic	Orthorhombic
Proportion present (%)				
Range	35–65	10–40	0–15	5–15
Average in ordinary cement	50	25	8	8
Rate of reaction with water	Medium	Slow	Fast	Medium
Contribution to strength				
Early age	Good	Low	Good	Good
Ultimate	Good	High	Medium	Medium
Heat of hydration	Medium	Low	High	Medium
Typical (cal/g)	120	60	320	100

supersaturated in calcium hydroxide (CH) and hydrated calcium sulfate ($C\bar{S}H$) until the reaction involving the formation of calcium sulfoaluminate removes most of the calcium sulfate from solution. The CH, however, remains in solution, and solid CH is present at all stages of the cement setting reactions.

Since the hydration of tricalcium silicate (C_3S) is the dominating mechanism in the overall hydration process, several distinct stages in its hydration have been identified (Kondo and Daimon 1969; Young 1972, 1976). These stages are shown in the conduction calorimetry curve in Figure 1. During Stage I, the initial hydrolysis of C_3S occurs, with a rapid release of heat and calcium hydroxide into solution. This leaves a C_3S particle with an approximately 10-nm insulating rind of hydrated C_3S.

In Stage II the release of CH continues, but at a slower rate limited by the ability of CH to interact with available water through the rind. The

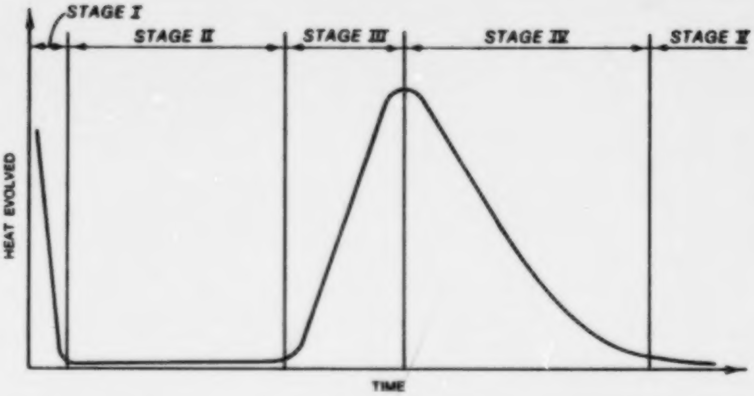


Figure 1. Heat liberation curve by hydrating tricalcium silicate as determined by isothermal calorimetry (Source: Kondo and Daimon 1969).

thin layers of hydrated calcium silicate (C-S-H) that make up the rind are probably a polymerization of the hydrolyzed silicate groups. Stage III is represented by an accelerated C_3S crystallization and the initiation of calcium hydroxide crystallization. Simultaneously, a transformation of the C-S-H gel occurs, exposing additional surface area of the anhydrous particle. Deceleration of these diffusion-controlled reactions typifies Stages IV and V, which continue as slowing exothermic reactions.

Hydration of tricalcium aluminate (C_3A), while not being critical to strength development, is crucial in determining cement set time and other Stage I and II characteristics (Hansen 1959). Hydration of C_3A in the absence of sulfate ions can be represented by the following equation:

$$2C_3A + 21\,H \longrightarrow C_4AH_{13} + C_2AH_8 \xrightarrow{\text{slow}} 2C_3AH_6 + 9H \qquad (1)$$

(metastable hexagonal hydrates) (stable hydrate)

The heat liberated in Equation 1 is sufficient to speed up the reaction to the stable form, C_3AH_6. Portland cement does, however, contain a small amount of sulfate as calcium sulfate (gypsum). This alters the hydration to the form of

$$C_3A + 3C\bar{S}H_2 + 26H \longrightarrow C_3A\cdot 3C\bar{S}\cdot H_{32} \qquad (2)$$

(ettringite)

The addition of 26 water molecules during the formation of ettringite brings about a corresponding volume increase. When ettringite forms early in the solidification process, the additional space is not a problem; it even develops binding properties that contribute to the early strength of the product. This phenomenon can actually be used to bind large amounts of sulfate in a solidification product by using clay-rich (alumina) binders. However, if the ettringite forms after solidification, the additional space required loosens the structure and causes an observable increase in permeability with a concomitant loss in strength (Wiedemann 1982). After a period of time, the length of which depends on the alumina-to-sulfate ratio of the cement, the ettringite crystals may react with C_2A according to

$$4H + 2C_2A + \underset{\text{(ettringite)}}{C_3A\cdot 3C\bar{S}\cdot H_{32}} \longrightarrow \underset{\text{(monosulfoaluminate)}}{3C_3A\cdot C\bar{S}\cdot H_{32}} + 4H \qquad (3)$$

Monosulfoaluminate in Portland cement concrete makes the concrete vulnerable to sulfate attack.

The major constituents of fully hydrated cement paste are discussed below.

1. Calcium silicate hydrate (C-S-H) makes up 50 to 60 percent of the volume of solids in fully hydrated Portland cement paste. Termed a C-S-H gel in older literature, this ill-defined compound forms small, poorly defined crystalline fibers in a reticular network.
2. Calcium hydroxide crystals constitute 20 to 25 percent of the volume of solids in the fully hydrated paste; it tends to form large crystals with distinctive hexagonal-prism morphology. The presence of significant amounts of calcium hydroxide makes the concrete reactive to acidic solutions.
3. Calcium sulfoaluminates make up 15 to 20 percent of the solids volume in the fully hydrated paste but appear to play a minor role in the structure and properties of the final product.

Voids in Hydrated Cement and Concrete

The several kinds of voids in hydrated cement paste have great influence on its final properties of strength, durability, and permeability. The smallest voids, which occur within the C-S-H gel structure, are 0.5 to 2.5 nm in diameter. They account for about 28 percent of the porosity in solid C-S-H. These small voids have little effect on the strength and permeability of the final product but appear to be important in drying shrinkage and creep.

Capillary voids account for the larger spaces which are not filled by solid components. In well-hydrated, low water/cement ratio mixes, capillary voids range from 10 to 50 nm, but in high-ratio mixes they may be as large as 3,000 to 5,000 nm. It is generally held that pore size distribution, and not simply total capillary porosity, is a better criterion for evaluating the characteristic of a cementitious product. Capillary voids larger than about 50 nm are thought to be detrimental to strength and permeability, while voids smaller than 50 nm are more important to drying shrinkage and creep. Capillary voids limit the strength of concrete by acting as "stress concentrators" (Hirsh et al. 1983).

The third type of voids, usually called "air voids," are generally spherical and usually range from 0.05 to 0.2 mm but may range up to 3 mm. Air voids are usually introduced intentionally into the hydrated cement paste to increase the resistance of the final product to freeze-thaw (frost) damage even though they typically adversely affect its strength and permeability.

Depending on the environmental conditions, the voids are capable of holding large amounts of water. Capillary water (in voids 5 nm or larger) is bulk water that is largely free from attractive surface forces. Water in voids greater than about 50 nm is considered free-water since its loss causes no shrinkage in the final product, while loss of water held by capillary tension in voids from about 5 to 50 nm may cause some shrinkage. Changes in the amount of capillary pore space with degree of hydration are illustrated in Figure 2a for a cement paste with a water/cement ratio of 0.66 and in Figure 2b for fully hydrated pastes of different water/cement ratios.

Absorbed water is close to the surface (probably within 1.5 nm of the surface) and held by hydrogen bonding and Van der Wal forces. Loss of absorbed water, even in air of 30-percent relative humidity, is mainly responsible for the shrinkage and cracking of the solidifying mass. The water more tightly bound in the interlayers of the C-S-H structure will be lost only in air with relative humidities below about 10 percent. The loss of water from the C-S-H structure will cause considerable drying shrinkage.

POZZOLANIC MATERIALS

By definition, pozzolans are materials that display no cementing actions by themselves but which contain constituents that combine with lime at ordinary temperatures and in the presence of water to form cementitious compounds. At present, the main pozzolans used commercially are fly ash from coal-fired power plants and kiln dust from lime or cement kilns. Fly ash is the fine ash produced by combustion of powdered coal with forced draft. The ash is carried up in the flue gases and collected in special equipment such as electrostatic precipitators or bag houses. Fly ash was first reported in the literature in terms of its pozzolanic properties in 1937 (Davis et al. 1937).

Most traditional literature is concerned with fly ash as an admixture in cement rather than as an independent pozzolanic material. Minnick (1967) investigated eight U.S. fly ashes and their reactions with hydrated lime over reaction periods up to 32 weeks. Minnick has suggested pozzolanic reactions according to the following:

$$\mathrm{CH} + \mathrm{S} \xrightarrow{H_2O} \mathrm{C_xS_yH_z} \qquad (4)$$

(C-S-H of varying stoichiometry)

$$\mathrm{CH} + \mathrm{A} \xrightarrow{H_2O} \mathrm{C_xA_yH_z} \qquad (5)$$

(hexagonal and cubic aluminate hydrates)

$$\mathrm{CH} + \mathrm{A} + \mathrm{S} \xrightarrow{H_2O} \mathrm{C_xA_yS_zH_w} \qquad (6)$$

(hydrogarnets)

$$\mathrm{CH} + \bar{\mathrm{S}} + \mathrm{A} \xrightarrow{H_2O} \mathrm{C_xA_y(C\bar{S})_zH_w} \qquad (7)$$

(ettringite and derivatives)

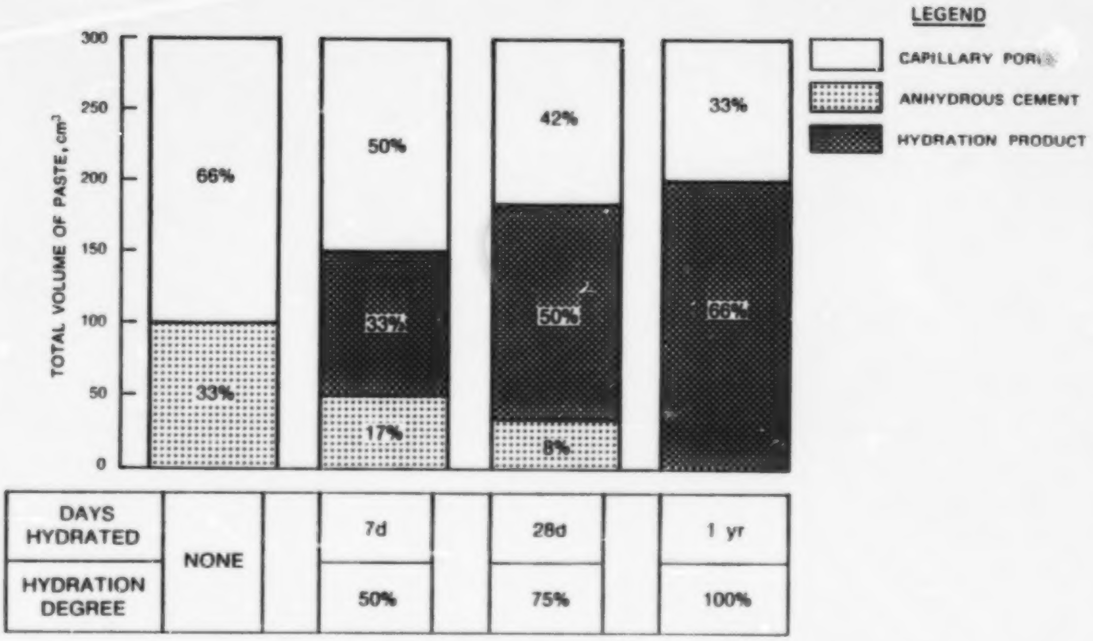


Figure 2a. Change in the amount of capillary pore space with degree of hydration for a cement paste with a 0.66 water/cement ratio (after Mehta 1987)

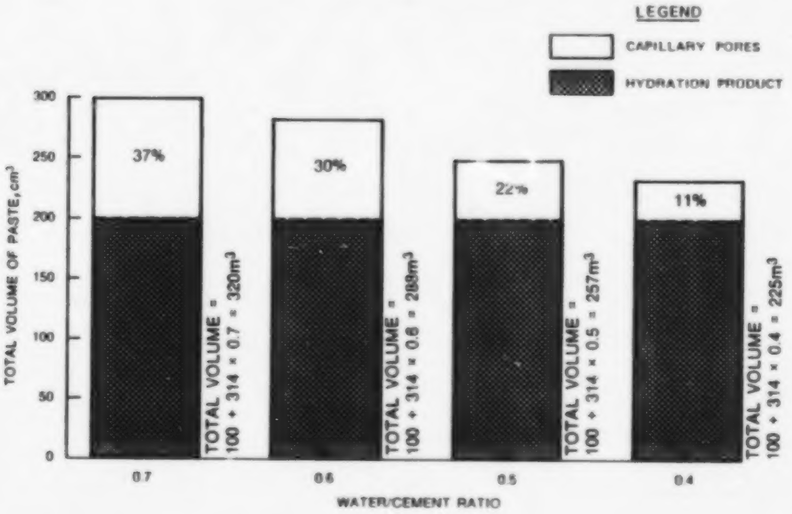


Figure 2b. Change in the amount of capillary pore space for a fully hydrated cement paste with differing water/cement ratios, based on equal amounts of Portland cement (after Mehta 1987)

The above reactions yield products whose properties are similar to the reaction products of Portland cement. One primary difference is that pozzolanic reactions consume lime rather than produce it, as with typical Portland cement hydration. This is an important factor in sulfate corrosion resistance and in differences in the effects of additives on the two S/S materials.

Pozzolanic reactions, while not identical, are similar to Portland cement reactions. The strength of products produced in both processes results from the formation of hydrated calcium silicates (C-S-H); however, pozzolanic reactions are not pure hydration reactions like those of Portland cement. Portland cement involves two or more solid phases plus water. Pozzolanic reactions generally are much slower than cement reactions, and set times are usually measured in days or weeks instead of hours.

THE STRENGTH-POROSITY RELATIONSHIP

Factors that influence the strength of a cement on pozzolanic mass are listed in Table 2. By far the most important factor is the water/cement ratio-porosity relationship. This is usually explained as the natural consequence of the weakening of the cement matrix caused by increasing porosity with increasing water/cement ratios (as discussed above, see especially Figure 2b). Typical data illustrating this point are shown in Table 3. Figure 2b also illustrates the increase in strength with increasing hydration (time of cure) which corresponds to a decrease in the total pore space.

TABLE 2. PRINCIPAL FACTORS AFFECTING STRENGTH OF CONCRETE AND STABILIZED/SOLIDIFIED WASTE

- Matrix Porosity
  - Water/cement ratio
  - Degree of hydration
    - Curing time
    - Temperature
    - Humidity
  - Mineral admixtures
  - Air content

- Specimen Parameters
  - Geometry
  - Dimensions
  - Moisture

- Chemical Interactions with Waste
  - Waste constituents
  - Cement and waste loading

- Stress Parameters
  - Stress type
  - Rate of application

TABLE 3. INFLUENCE OF WATER/CEMENT RATIO AND DEGREE OF HYDRATION ON CONCRETE STRENGTH

Water/cement ratios by weight	Unconfined compressive strength (psi) after different lengths of cure			
	1 day	3 days	7 days	28 days
0.35	1,300	2,900	4,450	6,300
0.45	900	2,200	3,500	5,250
0.55	550	1,650	2,750	4,350
0.65	300	1,200	2,000	3,450
0.75	200	950	1,550	2,800

Source: Portland Cement Association 1968.
Notes: Cylinders (6 by 12 in.) (15 by 30 cm) of normal type I cement undergoing moist-cure. To convert pounds (force) per square inch to megapascals, multiply by 0.006894757.

Water/Cement Ratio and Degree of Hydration

The relationship between porosity and strength is of great importance to the prediction of the ability of a given waste-cement mixture to contain the contaminants when subjected to various environmental conditions. Therefore, compressive strength may be an indicator of the S/S waste's resistance to leaching. This thought is further developed below in the section on durability-permeability.

Mineral Admixtures

The use of pozzolanic and cementitious by-products such as fly ash, blast furnace slag, or kiln dusts as admixtures is an important issue in waste S/S. When used in addition to, or as a partial replacement for Portland cement, the presence of the mineral generally retards the rate of strength gain. However, the mineral admixture reacts with the excess calcium hydroxide present in the hydrated Portland cement to form additional C-S-H and leads to a significant reduction in porosity and ultimate strength gain in the final product (Marsh et al. 1985). Consequently, considerable improvement in the ultimate strength and impermeability (water tightness) can be achieved by their incorporation.

Air Entrainment

Additives causing stable air incorporation into the cement paste are universally deleterious to the ultimate strength and impermeability of the concrete, due most likely to the added large-pore space. However, the entrained air increases the resistance of the products to freezing.

Specimen Parameters

The standard test specimen for the uniaxial compression test in the United States (ASTM C 469) is a right cylinder of 6 in. (15 cm) diameter (d) and 12 in. (30 cm) height (h) (ratio h/d = 2). Measured strengths vary indirectly with h/d ratio, with a h/d ratio of 1 giving 15 to 20 percent higher strength and a ratio of 4 about 10 percent less. Specimens of different sizes, but having a h/d = 2 , have different measured strengths. A 3- by 6-in. (7- by 15-cm) cylinder has about 6 percent higher strength, and a 9- by 18-in. (23- by 46-cm) specimen has about 10 percent lower strength than the standard 6- by 12-in. cylinder.

Strength tests based upon the 6-in. standard test cube, which are common in European countries, generally indicate strengths 10 to 15 percent higher than tests of the same material using 6- by 12-in. cylinder. Similarly, the use of a 2-in. cube for compressive strength testing would be expected to give 15 to 25 percent higher strength values for the same cement mixtures.

Concrete products also perform differently under different stresses, compressive strength being the outstanding feature of structural concrete. Most designs emphasize compressive strength, since the tensile strength of concrete is usually an order of magnitude lower. The rate of stress application is also important, as long-term stress brings on creep strain due to moisture movement in the C-S-H voids and the development of microcracks.

Chemical Interaction of Waste with the Cement Binder

Wastes most amenable to S/S are usually water-based sludges containing a wide variety of inorganic and organic constituents at different and varying concentrations. Predicting the effect of these poorly defined mixtures on the strength of hydrating cement paste without benefit of bench- or pilot-scale studies is complex at best and probably beyond the state of the art.

THE DURABILITY-PERMEABILITY RELATIONSHIP

Long-term durability of the S/S waste product is a prime consideration in the design and specification of waste S/S systems. Prediction of long-term integrity of the final waste form requires consideration of all possible modes of failure (Table 4). For cementitious S/S products, water is generally involved in every form of deterioration; in porous solids, permeability of the material to water usually determines the rate of deterioration. Internal movement and changes in the structure of water are known to cause disruptive volume changes of many types. Examples are freezing of water into ice, formation of ordered structure of water inside fine pores, development of osmotic pressures due to different ionic concentrations, and hydrostatic pressure buildup by differential vapor pressures. All of these can lead to large internal stresses within a moist solid and result in its ultimate failure.

In porous solids, water also acts as a vehicle for transport of solutes through the material, both aggressive ions into and waste materials out. A discussion of permeability is therefore of basic interest to an understanding of both durability and leachability. Permeability of concrete products depends primarily on the water/cement ratio (which determines the size, volume, and continuity of capillary voids) and the development of microcracks that occur between the cement paste and the surface of included solids (such as aggregates or waste solids). The suspended particulates in waste sludges (acting as small aggregate) are typically very small. In general, the smaller

TABLE 4. PHYSICAL CAUSES OF DETERIORATION OF CONCRETE PRODUCTS

- Surface Wear
  - Abrasion
  - Erosion
  - Cavitation

- Cracking
  - Volume changes
    - Moisture gradients and humidity
    - Crystallization pressures of salts in pores
  - Exposure to temperature extremes
    - Freeze-thaw action
    - Fire
  - Structural loading
    - Overload or impact
    - Cyclic loading

the suspended particles, the fewer the microcracks at their surface, and the lower the overall permeability of the final product. The primary consideration of permeability of S/S waste sludges of small particle size then, is the water/cement ratio.

Cracking by Crystallization of Salts in Pores

Stabilization/solidification waste products often contain substantial amounts of salts and/or organic molecules with appreciable water solubilities. Concentration of these materials at or below the surface of the solid where evaporation of pore water is occurring can cause the development of supersaturated solutions and the formation of salt crystals in the pores of the S/S product.

Crystallization occurs only when the concentration of the solute (C) exceeds the saturation concentration (Cs) at a given temperature. Generally, the higher the degree of supersaturation (the ratio of C/Cs), the greater the crystallization pressure exerted on the solid structure. Table 5 presents crystallization pressures for C/Cs = 2 of a series of salts that are common in stone and concrete materials. These values were calculated by Winkler (1975) in an effort to understand the rapid deterioration of stone and concrete monuments by smog and acid (high-sulfate) rain. For example, at C/Cs = 2 , halite (NaCl) at 25° C produces 605 atm (61 MPa) of pressure, and at C/Cs = 10 , 2,020 atm (205 MPa). These pressures are strong enough to disrupt the structure of the stone or concrete products which contain these constituents. As seen in Table 5, common salts have a wide range of crystallization pressures. Due to the wide variety of materials found in hazardous wastes, this effect can be appreciable.

Damage typical of this effect is the powdering or spalling of the subsurface of the solid material which progressively deepens into the material as

TABLE 5. CRYSTALLIZATION PRESSURES FOR SALTS

Salt	Chemical Formula	Pressure (atm)* $C/C_s = 2$ 0° C	50° C
Anhydrite	$CaSO_4$	335	398
Bischofite	$MgCl_2 \cdot 6H_2O$	119	142
Dodekahydrate	$MgSO_4 \cdot 12H_2O$	67	80
Epsomite	$MgSO_4 \cdot 7H_2O$	105	125
Gypsum	$CaSO_4 \cdot 2H_2O$	282	334
Halite	$NaCl$	554	654
Heptahydrite	$Na_2CO_3 \cdot 7H_2O$	100	119
Hexahydrite	$MgSO_4 \cdot 6H_2O$	118	141
Kieserite	$MgSO_4 \cdot H_2O$	272	324
Mirabilite	$Na_2SO_4 \cdot 10H_2O$	72	83
Natron	$Na_2CO_3 \cdot 10H_2O$	78	92
Tachhydrite	$2MgCl_2 \cdot CaCl_2 \cdot 12H_2O$	50	59
Thenardite	Na_2SO_4	292	345
Thermonatrite	$Na_2CO_3 \cdot H_2O$	280	333

Source: Winkler (1975).
* To convert atmospheres (standard) to megapascals, multiply by 0.101325.

its porosity increases. Damage to S/S products due to wet-dry cycles may be to a large extent due to the cyclic dissolution and crystallization of contained salt.

Wet-Dry Cycling

Other than cracking by salt crystallization as described above, wet-dry cycling of normal concrete products does not usually produce significant damage to its structure. However, as the total proportion of cement is reduced or the water/cement ratio is increased, as is common in waste S/S practice, wet-dry cycling may cause rapid deterioration of the S/S waste product. Jones and Malone (1982) reported rapid deterioration of S/S inorganic waste products produced by commercial S/S vendors using ASTM standard test procedure D559-57 for compacted soil-cement mixtures (ASTM 1976).

Freeze-Thaw Damage

Although there is generally a direct relationship between strength and durability, this does not hold in the case of frost damage. In an analogous manner to salt crystals, formation of ice crystals at subfreezing temperatures can cause rapid deterioration of water-saturated concrete products.

The freezing of water increases its volume by approximately 9 percent. When freezing in a capillary void, the added volume produces large stresses on the concrete structure unless the excess water can flow into larger voids as the specimen freezes. The hydraulic pressure generated by freezing pore water depends upon the permeability of the material, the distance from the surface (escape boundary), and the rate at which ice is formed (Powers 1958). Disruptive pressures will result unless every capillary pore is no further than about 0.1 mm from the nearest escape boundary.

Durability of concrete products to freeze-thaw cycles can be provided by entraining small air bubbles into the cement paste which provide water escape boundaries. Small amounts of certain air-entraining agents added to the cement paste (e.g., 0.05 weight percent of cement) will bring about the incorporation of stable, 0.05- to 1-mm bubbles in the final product. For a given volume of air, depending upon the size of the voids, the number of voids, and void spacings, the degree of protection against freezing damage can vary a great deal. This is illustrated in Table 6. However, in medium- and high-strength concretes, every 1-percent increase in the air content reduces the ultimate strength of the final product by about 5 percent.

TABLE 6. DURABILITY TO FREEZE-THAW CYCLES OF NEAT CEMENT SAMPLES WITH DIFFERENT NUMBERS OF AIR BUBBLES

Air voids/cm^3	Total air volume (%)	Freeze thaw cycles to show 0.1% expansion
24,000	5-6	29
49,000	5-6	39
55,000	5-6	82
170,000	5-6	100
800,000	5-6	550

Source: Woods (1968).

The degree of water saturation also affects freeze-thaw damage. There is a critical degree of saturation above which concrete is likely to crack and spall when exposed to very low temperatures, usually between 80- and 90-percent saturation. Below the critical degree of saturation, freeze-thaw damage does not usually occur. A concrete product may fall below the critical degree of saturation after adequate curing, but depending on the permeability, it may again reach or exceed the critical degree of saturation in a short time when exposed to a moist environment. Also, as a rule of thumb, the higher the water/cement ratio, or the lower the degree of hydration, the greater the amount of freezable water that will be present at any given temperature and humidity.

Deterioration by Chemical Reactions

The effects on S/S waste products of internal waste constituents as well as external aggressive agents must be adequately known before the long-term stability of the S/S product can be assumed. The solid phase of a well-hydrated Portland cement paste exists in a stable equilibrium with the high-pH pore fluid. High concentrations of Na+, K+, and OH-ions bring about a pH of 12.5 to 13.5 in the pore fluid.

In principle, any environment where the pH is less than 12.5 could be considered an aggressive one because any reduction of alkalinity in the pore fluid will eventually lead to destabilization of the principal cementitious hydration products. The rate of chemical attack on the S/S waste product is a function of the pH of the external fluid, its buffering capacity, and the permeability of the S/S product. In general, pH levels above 6 cause such a slow reaction that they can be neglected. However, natural CO_2, sulfates, and chlorides common in ground- and rain-waters may result in aggressive solutions below pH 6, which can be detrimental to the S/S waste product.

Cation-exchange reactions can occur between the external solution and the cement binder. Anions in acidic solutions that form soluble calcium salts, such as calcium chloride, acetate, and bicarbonate, will cause the calcium in the S/S product to be removed by leaching. This is particularly damaging because it increases the permeability of the concrete, which increases the rate of further exchange reactions. Certain anions form nonexpansive, insoluble calcium salts such as calcium oxalate, tartrate, phosphate, or humic acid salts. As these salts are only slightly soluble in water, they do not cause much damage to the concrete. Magnesium salts may exchange with calcium in the cement binder, eventually reacting with the C-S-H to break down the fundamental cementitious matrix of the cement and cause breakdown of the S/S structure.

Sulfate attack of concrete products has been a serious and well-known problem for many years and is a serious consideration in the S/S of sulfate-containing wastes in Portland cement. Concentrations of soluble sulfates greater than 0.1 percent in soil or 150 mg/ℓ in water will endanger concrete products, and soils of over 0.5 soluble sulfates or over 2,000 mg/ℓ in water can have serious effect.

The most common reaction in sulfate attack is the reaction of both alumina-containing hydrates ($C_3A \cdot 3C\bar{S} \cdot H_{18}$ and $C_3A \cdot CH \cdot H_{18}$) with sulfate and calcium hydroxide to produce ettringite ($C_3A \cdot 3C\bar{S} \cdot H_{32}$), which forms expansive crystals that break up the final S/S product. Use of Portland cement containing less than 5 percent C_3A (ASTM Type V) will overcome the effects of moderate sulfate exposure. Cements that contain little or no calcium hydroxide (e.g., high alumina cements or Portland cement with more than 70 percent blast-furnace slag or with at least 25 percent pozzolan) will withstand very high sulfate conditions. Pozzolanic S/S systems are also useful for S/S of high-sulfate wastes since they do not contain free calcium hydroxide and thus are thought to be less reactive to sulfate.

Effects of Radiation

Large doses of gamma radiation do not appear to affect setting properties or cause appreciable loss of strength or increased leachability in Portland cement solidified waste products (Neilson et al. 1987). Waste forms produced with 15.6 wt%, fully loaded (with radioactive cesium and strontium) resin beads, 21.7 percent water, and 62.7 percent Portland type I-II cement were subjected to high doses of gamma irradiation (4.0 to 5.7 × 10^8 rads) and subjected to testing. Results of the tests are presented in Table 7.

TABLE 7. STABILITY OF PORTLAND CEMENT SOLIDIFIED WASTES TO HIGH DOSES OF GAMMA RADIATION

Attribute	Waste*	Control	Irradiated (5×10^8 rads)
Compressive strength (psi)			
	PF-7	20,200 ± 3,300	25,100 ± 9,900
	PF-24	25,000 ± 5,000	22,800 ± 11,800
Leachability index** for ^{134}Cs and ^{137}Cs (averaged)			
Distilled water	PF-7	10.3	9.35
Distilled water	PF-24	10.5	10.0
Sea water	PF-7	9.6	10.0
Sea water	PF-24	10.4	10.9

* Fully loaded resin beads from prefilter no. 7 or no. 24.

** Leachability index is negative log of leaching rate (larger numbers leach less) (see American Nuclear Society (ANS) 1986).

SECTION 4

EFFECTS OF STANDARD ADMIXTURES ON PORTLAND CEMENT/POZZOLAN PRODUCTS

INTRODUCTION

The properties of concrete in both the fresh and hardened state are typically modified by adding specific materials to the concrete mixtures. The additives, generally called admixtures, vary widely in chemical composition and may modify more than one property of the concrete mixture. It has been estimated that 88 percent of concrete placed in Canada and 70 percent placed in the United States includes one or more admixtures (Mehta 1987).

An understanding of the effects of common, well-studied admixtures gives a basis for assessing the possible range of effects of the S/S waste constituents on the concrete or pozzolanic matrix. American Concrete Institute (ACI) Committee 212 report Admixtures for Concrete (1963) contains a thorough report on the various effects of standard admixtures in concrete production, and ASTM Standard C 494-82 covers chemical admixtures for concrete (ASTM 1982). Vivian (1960) has written an excellent review of early work in this field. Rixon (1978), Schutz (1983), and Ramachandran (1984) have written more recently on chemical admixtures.

Admixtures fall broadly into three categories: 1) surface active molecules that work on the cement-water system immediately upon addition by influencing the surface tension of water and by absorbing onto the surface of cement particles; 2) set-controlling materials that ionize and affect the chemical reaction between the cement and the water only after several minutes or hours; and 3) finely ground, insoluble minerals, either natural materials or by-products, which immediately affect the rheological behavior of the fresh concrete, but whose chemical effects take several days or months to manifest themselves. A summary of commonly used concrete admixtures, and the applicable ASTM specifications, is given in Table 8.

Many admixture operations are dependent upon the conditions under which the admixtures are applied. For instance, triethanolamine has been shown to retard the hydration of C_3S but to accelerate the hydration of C_3A (Ramachandran 1976a). Lignosulfonate acts as a set retarder and, in the proper dosages, also increases strength (Young 1972). Admixture dosage is critical if the desired effects are to be attained. Parameters such as water content of the concrete formulation also play an important role. For example, amines and amino acids show accelerating properties at low water content, but become retarders if the water content is sufficiently increased.

SURFACE-ACTIVE CHEMICALS (SURFACTANTS)

Surface active molecules are those which lower the surface tension of water; examples are soaps and detergents. See Camp et al. (1985) for a general discussion of surfactants. Two major uses of surfactants as concrete

TABLE 8. COMMONLY USED CONCRETE ADMIXTURES

Primary function	Principal active ingredients/ ASTM specifications	Side effects
Water-reducing		
Normal	Salts, modifications and derivatives of lignosulfonic acid, hydroxylated carboxylic acids, and polyhydroxy compounds. ASTM C 494 (Type A).	Lignosulfonates may cause air entrainment and strength loss; Type A admixes tend to be set-retarding when used in high dosage.
High range	Sulfonated naphthalene or melamine formaldehyde condensates. ASTM C 494 (Type F).	Early slump loss; difficulty in controlling void spacing when air entrainment is also required.
Set-controlling		
Accelerating	Calcium chloride, calcium formate, and triethanolamine. ASTM C 494 (Type C).	Accelerators containing chloride increase the risk of corrosion of the embedded metals.
Retarding	Same as in ASTM Type A; compounds such as phosphates may be present. ASTM C 494 (Type B).	
Water-reducing and set-controlling		
Water-reducing & retarding	Same as used for normal water reduction. ASTM C 494 (Type D).	(See Type A above.)
Water-reducing & accelerating	Mixtures of Types A and C. ASTM C 494 (Type E).	(See Type C above.)
High-range water-reducing & retarding	Same as used for Type F with lignosulfonates added. ASTM C 494 (Type G).	(See Type F above.)

(Continued)

TABLE 8. (Concluded)

Primary function	Principal active ingredients/ ASTM specifications	Side effects
Workability-improving		
Increasing consistency	Water-reducing agents, [e.g., ASTM C 494 (Type A)].	(See Type A above.)
Reducing Segregation	(a) Finely divided minerals (e.g., ASTM C 618).	Loss of early strength when used as cement replacement.
	(b) Air-entrainment surfactants (ASTM C 260).	Loss of strength.
Strength-increasing		
By water-reducing admixtures	Same as listed under ASTM C 494 (Types A, D, F, and G).	(See Types A and F above.)
By pozzolanic & cementitious	Same as listed under ASTM C 618 and C 989.	Workability and durability may be improved.
Durability-improving		
Frost action (air entraining)	Wood resins, proteinaceous materials, and synthetic detergents (ASTM C 260).	Strength loss.
Thermal cracking Alkali-aggregate expansion Acidic solutions Sulfate solutions	Fly ashes and raw or calcined natural pozzolans (ASTM C 618); granulated and ground iron blast-furnace slag (ASTM C 989); condensed silica fume; rice husk ash produced by controlled combustion. (High-calcium and high-alumina fly ashes, and slag-Portland cement mixtures containing less than 60% slag may not be sulfate resistant.)	Loss of strength at early ages, except when highly pozzolanic admixtures are used in conjunction with water-reducing agents.

Adapted from Mehta (1987).

admixtures are for reduction of the proportion of water in concretes (water-reducing admixtures) and for introducing large numbers of small air bubbles into the concrete mix (air-entrainment admixtures).

The materials that have been described and are generally available for use as water-reducing admixtures and set-controlling admixtures fall into five general classes:

1. Lignosulfonic acids and their salts.
2. Modifications and derivatives of lignosulfonic acids and their salts.
3. Hydroxylated carboxylic acids and their salts.
4. Modifications and derivatives of hydroxylated carboxylic acids and their salts.
5. Other materials, which include:
    (a) Inorganic materials, such as zinc salts, borates, phosphates, chlorides.
    (b) Amines and their derivatives.
    (c) Carbohydrates, polysaccharides, and sugar acids.
    (d) Certain polymeric compounds, such as cellulose ethers, melamine derivatives, naphthalene derivatives, silicones, and sulfonated hydrocarbons.

These admixtures can be used either alone or in combination with other organic or inorganic materials.

Water-Reducing Surfactants

When water is added to cement, the mixture does not become well dispersed because of the high surface tension of the water and the tendency of the cement particles to adhere and form flocs due to the attraction of oppositely charged edges of the cement particles. Water-reducing surfactants, or plasticizing surfactants, act by adsorbing to the surface charges of the cement particles so that the surface of the particle becomes hydrophilic and no longer attracted to other cement particles. Typical examples are citric acid, gluconic acid, and lignosulfonic acid. A better dispersed suspension of the cement paste means that 1) at a given water-cement ratio, the cement paste has a higher consistency and pumpability, 2) a lower water/cement ratio can be used to increase strength and lower permeability without a change in consistency, and 3) less cement can be used in the mix at the same water-cement ratio (more aggregate or waste loading).

Superplasticizers, sometimes called high-range water-reducing admixtures, are 3 to 4 times as effective as normal water-reducing admixtures (Malhotra 1979). They are long carbon-chain, high molecular weight anionic surfactants with a large number of polar groups. Adsorbed onto the cement particles, superplasticizers import a strong negative charge to their surface which helps lower the surface tension of surrounding water and greatly increases the fluidity of the system. The better dispersion of the cement particles does tend to cause their more rapid hydration, increasing the rate of set. Set retardants are sometimes added to offset this effect.

Water reducing admixtures may be useful in waste S/S with cement. The 5- to 10-percent water reduction made possible with normal plasticizers, or the 25- to 30-percent water reduction with superplasticizers, increases the compressive strength and decreases the amount of void space and therefore the permeability of the final product for a given amount of cement. A more leach resistant and durable S/S waste product should result.

Air-Entraining Surfactants

These materials differ from the water-reducing surfactants in that the molecule contains a nonpolar portion along with the anionic, polar group. The surfactants coat the surface of small air bubbles and stabilize them so that they do not coalesce and separate from the concrete during mixing or setting. They also coat the charged surfaces of the cement particles, causing them to become hydrophobic, which can cause a lower rate of hydration (delayed setting) at higher doses. Doses of 0.05 percent by weight of cement are often sufficient to incorporate 0.05- to 1-mm bubbles into the cement. Air contents of 3 to 8 percent of the total mix are recommended for the production of frost-resistant concretes, depending upon the size of aggregates (larger aggregates require less entrained air) and the degree of exposure (more severe exposure requires more air entrainment).

SET-CONTROLLING CHEMICALS

The early events in the setting and hardening of concrete involve the dissolution, ionization, and hydration of sparingly soluble chemical components. Any added soluble chemical that interferes with any of these processes may delay or accelerate the rates of hydration of the various cement components, depending on its relative effect on all of the components present.

Hydrating cement mixtures are composed primarily of acidic anions (silicate and aluminate) and a base cation (calcium). The solubilities of each of these ions is dependent upon the concentrations of the other ions in solution. Since most chemical admixtures which affect the rate of hydration of cement pastes ionize in water solution, their presence is believed to alter the type and concentrations of the ionic constituents in the solution phase, which influences the dissolution and crystallization of the cement compounds. The following guidelines are proposed by Joisel (see Mehta 1987):

1. Accelerators must promote the dissolution of the calcium cations and anions from the cement particles. The most effective accelerator would promote the dissolution of the least soluble constituent (silicate).

2. Retarding admixtures must interfere with the dissolution cations (calcium) and anions, preferably that anion which has the highest rate of dissolution during early hydration (i.e., the aluminate ions).

3. A strong cation (e.g., K+ or Na+) will reduce the solubility of the calcium cation but will accelerate the solubility of the anions (silicate and aluminate). At lower concentrations the former effect is dominant; at the higher concentrations, the latter.

4. A strong anion (e.g., Cl^-, NO_3^-, or $SO_4^=$) reduces the solubility of the cement anions (silicates and aluminates) but tends to increase the mobility of the calcium cation. At low concentrations the former effect appears dominant; at higher concentrations, the latter.

From these considerations, it can be seen that the net effect of any admixture on the rate of hydration depends on the balance of its effect on the type and concentration of ions contributed by the admixture. For instance, small concentrations of the salt of a weak base and a strong acid (e.g., $CaCl_2$), or a strong base and a weak acid (e.g., K_2CO_3), will tend to retard the solubility of the calcium and aluminate ions. At higher concentrations, the accelerating effects of the increased solubilities of silicate and aluminate ions predominate, and the salts become accelerators.

Calcium chloride at 1 to 3 percent the weight of cement is the most common accelerator and has been widely studied (Ramachandran 1976b, 1984). Some of the properties of hydrating cement paste which are influenced by calcium chloride are summarized in Table 9. Other salts that accelerate cement paste hydration are sodium fluoride, aluminum chloride, sodium aluminate, and potassium carbonate. Setting time as short as 15 to 30 seconds can be obtained. Some ready-to-use mixtures have an initial set of 1 to 4 minutes with a final set of 3 to 10 minutes.

Organic acids and their weakly acid soluble salts act as accelerators because they increase the dissolution of calcium. Calcium formate and formic acid are common accelerators. Triethanolamine is an active accelerator because of its ability to accelerate the hydration of C_3A and the formation of ettringite; however, it also retards the hydration of C_3S and reduces the rate of strength development. Comparison of the development of strength and of setting times for some common accelerators is illustrated in Table 10.

Set retarders also work by other mechanisms. Surfactants such as gluconates and lignosulfonates delay bond formation among the hydration products, delaying crystallization (Hansen 1959, Young 1976). Other retarders such as sodium salts of phosphoric, boric, oxalic, and hydrofluoric acid form insoluble calcium salts which precipitate out and form insoluble and impermeable barriers around the cement particles. This slows hydration considerably and retards set and strength development.

Early strengths are lower in specimens with retarders than those in reference specimens, as would be expected. However, at longer periods the specimens containing retarders generally have higher compressive strength and comparable flexural strength (see Tables 11 and 12). The drying-shrinkages of specimens containing retarders are also comparable to those reference specimens without admixtures. Soluble calcium salts which may provide anions that adsorb onto the calcium hydroxide crystal surfaces cause a retarding effect (e.g., calcium nitrate).

Scholer (1975) studied the effects of 65 different chemical compounds and three ASTM Type D admixtures on the fresh and hydrated condition of cement pastes. Setting time, molecular configuration related to the effectiveness of the retarders, oven-dry shrinkage, nonevaporable water, and specific surface area were determined for each admixture. Long-term shrinkage of concrete was

TABLE 9. SOME OF THE PROPERTIES INFLUENCED BY THE USE OF CALCIUM CHLORIDE ADMIXTURE IN CONCRETE

Property	General effect	Remarks
Setting	Reduces both initial and final setting	ASTM standard requires that initial and final setting times should occur at least 1 hour earlier with respect to reference concrete.
Compressive strength	Increases significantly the compressive strength in the first 3 days of curing (gain may be about 30-100%).	ASTM requires an increase of at least 125% over control concrete at 3 days. At 6-12 months, requirement is only 90% of control specimen.
Tensile strength	A slight decrease at 28 days.	
Flexural strength	A decrease of about 10% at 7 days.	This figure may vary depending on the starting materials and method of curing. The decrease may be more at 28 days.
Heat of hydration	An increase of about 30% in 24 hours.	Total amount of heat at longer times is almost the same as that evolved by reference concrete.
Resistance to sulfate attack	Reduced	Can be overcome by use of Type V cement with adequate air entrainment.
Alkali-aggregate reaction	Aggravated	Can be controlled by use of low-alkali cement or pozzolana.
Corrosion	Causes no problems in normal reinforced concrete if adequate precautions taken. Dosage should not exceed 1.5% $CaCl_2$, and adequate cover to be given. Should not be used in concrete containing a combination of dissimilar metals or where there is a possibility of stray currents.	Calcium chloride admixture should not be used in prestressed concrete or in a concrete containing a combination of dissimilar metals. Some specifications do not allow use of $CaCl_2$ in reinforced concretes.

(Continued)

TABLE 9. (Concluded)

Property	General effect	Remarks
Shrinkage and creep	Increased	
Volume change	Increase of 0-15% reported.	
Resistance to damage by freezing and thawing	Early resistance improved.	At later ages may be less resistant to freezing and thawing.
Watertightness	Improved at early ages.	
Modulus of elasticity	Increased at early ages.	At longer periods almost same with respect to reference concrete.
Bleeding	Reduced	

Adapted from Mehta 1986, p 263.

TABLE 10. EFFECT OF ACCELERATORS TRIETHANOLAMINE, CALCIUM FORMATE, AND CALCIUM CHLORIDE ON THE RATE OF HARDENING AND COMPRESSIVE STRENGTH OF CONCRETE

Admixture	Rate of use (wt % of cement)	Compressive strength (psi)* 7-day	28-day	Time of final setting (hr)
None	--	4,810	6,710	12.0
Triethanolamine	0.025	5,160	6,670	9.7
None	--	4,430	6,130	12.4
$CaCl_2$	2.00	4,490	5,615	4.0
Calcium formate	0.05	4,630	6,275	8.9
Calcium formate	1.00	4,910	6,485	8.4
Calcium formate	1.50	5,200	6,585	7.6
Calcium formate	2.00	5,330	6,610	6.7

Source: Rosskopf, Linton, and Peppler 1975.

* To convert pounds (force) per square inch to megapascals, multiply by 0.006894757.

TABLE 11. COMPRESSIVE STRENGTH (CS) OF MORTARS CONTAINING RETARDERS

Retarder	Admixture (wt % of cement)	1 day CS	2 days CS	7 days CS	28 days CS	90 days CS
None	---	11.8	21.6	37.8	45.3	53.9
Sucrose	0.5	10.0	21.6	47.1	59.8	62.8
Sucrose	1.0	1.3	11.8	43.2	53.9	60.3
Glucose	1.0	7.1	23.7	36.8	53.4	58.8
Glucose	2.0	1.0	8.3	27.9	45.6	51.5
Phosphoric acid	0.5	7.1	18.1	48.1	60.8	71.1
Phosphoric acid	1.0	2.2	14.7	45.1	64.7	74.0
Phosphoric acid	2.0	1.2	12.3	44.1	60.3	69.6

Note: All values given in megapascals (1 MPa = 145 psi).

TABLE 12. FLEXURAL STRENGTH (FS) OF MORTARS CONTAINING RETARDERS

Retarder	Admixture (wt % of cement)	1 day FS	2 days FS	7 days FS	28 days FS	90 days FS
None	---	3.5	4.8	7.6	8.6	8.8
Sucrose	0.5	2.9	5.0	7.8	8.1	8.2
Sucrose	1.0	0.4	2.8	7.6	7.9	9.4
Glucose	1.0	2.0	4.9	6.7	7.5	7.9
Glucose	2.0	0.1	2.5	5.5	7.4	7.9
Phosphoric acid	0.5	1.8	4.2	7.6	8.3	8.1
Phosphoric acid	1.0	0.5	3.3	7.6	8.5	8.6
Phosphoric acid	2.0	0.2	3.2	7.7	7.5	8.0

Note: All values given in megapascals (1 MPa = 145 psi).

not appreciably affected. He concluded that strong retarders have a molecular composition that includes many oxygen atoms that are constrained to approach each other closely. Hydroxyl, carboxyl, and carbonyl are all affective, but carbonyl is especially strong in its influence on set time. These groups are presumed to exert a polarizing influence that contributes to the strong adsorption on the solid surfaces. More weakly electronegative atoms on the molecule do not have the same effect as oxygens.

The retarding effects of sugars on cement hydration were studied in detail by Thomas and Birchall (1983). They compared different sugars using solution analysis, colorimetry, calcium binding ability, and alkaline stability. The best retarders were sucrose and raffinose, which also have a remarkable ability to solubilize cement constituents and give rise to dramatic increases (10 to 20 times) in the amount of silica present in solution. However, no evidence for sucrose-silicate complexes was found using ^{13}C and ^{29}Si nuclear magnetic resonance (NMR) analysis. The authors relate the retarding action of sugars in terms of adsorption onto and the poisoning of hydrating surfaces.

MACRO-DEFECT-FREE (MDF) CEMENT PASTES

A new class of high-strength cement materials, called macro-defect-free (MDF) cements, achieves higher strengths by the absence of the relatively large voids or defects which are usually present in conventionally mixed cement pastes (Roy 1987). In this process, 4 to 7 percent of one of several water-soluble polymers, such as hydroxypropylmethyl cellulose, polyacrylamide, or hydrolyzed polyvinylacetate, is added as a rheological aid to permit cement to be mixed with very low water-cement ratios. Coupled with high-shear mixing, the method produces a plastic, cohesive mixture that can be shaped by extrusion or other forming techniques. Set times range from minutes to hours. The polymers also appear to be a significant structural component. Where ordinary cement mixtures have compressive strengths of around 40 MPa (5,800 psi), MDF cements can have a compressive strength as high as 100 to 300 MPa (14,500 to 43,500 psi).

MINERAL ADMIXTURES

Mineral admixtures are usually siliceous materials that are added to the cement mixtures in relatively high proportions, for example 15 to 100 percent of the weight of cement. Typical admixtures are pozzolanic (e.g., volcanic glass, silica fume, rice husk ash, and Class F fly ash), cementitious (granulated iron blast-furnace slag, hydraulic limes, and slag cements), or both (high-calcium Class C fly ash). Other non-setting mineral admixtures are finely divided quartz; siliceous sands; dolomitic and calcitic limestones; marble, granite, and other rock dusts; and hydrated dolomitic or high-calcium lime. Of these, fly ash, kiln dusts, and blast-furnace slags are by far the most commonly used mineral admixtures.

Pozzolanic Admixtures

Proposed minimum standards for fly ash used as a cement admixture are given by Idorn and Thaulow (1985). For Class F fly ashes, the major constituent, SiO_2, should comprise a minimum of 50 percent of the material by weight; Al_2O_3 should comprise 20 to 35 percent; and CaO, 2 to 8 percent. Between 60 and 85 percent of the volume of the fly ash should be noncrystalline or glass. Pozzolanic materials, by definition, react with hydrated calcium hydroxide to form C-S-H,

$$\text{Pozzolan} + \text{CH} + H_2O \xrightarrow{\text{slow}} 2\text{C-S-H}$$

while in Portland cement the reaction is

$$C_3S + 3H_2O \xrightarrow{\text{fast}} \text{C-S-H} + 2\text{CH}$$

The addition of pozzolan to Portland cement then slows the overall hydration rate of the mixture as the pozzolan reacts with the free lime (CH), which is liberated from the Portland cement hydration reaction. In consuming the free lime, the pozzolan has been shown to fill the large capillary spaces in which the calcium hydroxide crystals normally form, thus improving the strength and impermeability of the system. Reductions in permeability of up to 3 orders of magnitude are common (Marsh et al. 1985). The reduction in permeability resulting from pozzolan addition is thought to be the reason for lower leaching losses, although a certain amount of additional binding of heavy metals by the active silica (thus preventing their leaching) may be responsible for some of the effect (Coté and Webster 1987, Van der Sloot et al. 1987).

The setting and strength characteristics of Portland cement products containing Class C (high lime) fly ash were studied by Baker and Laguros (1985). Class C fly ash from western coal has not been studied to such an extent as Class F low-lime, eastern fly ash. They found that setting time and development of compressive strength were delayed, but after 1 week, the compressive strength of all mixtures containing Class C fly ash (at 20 to 50 percent replacement of cement) surpassed the cement-only controls. A decrease in the level of calcium hydroxide was not seen (as is typical for mixes with Class F fly ash). They suggested that the retardation mechanism may be associated with the high levels of ettringite formed early in the hydration process and its subsequent conversion to monsulfoaluminate. A simple heat of hydration test was presented to help explain the observed strength gains. High- and low-calcium fly ash-cement mixtures were also compared by Grutzeck et al. (1985), who found similar results, with high-calcium mixtures retarding early strength development to a larger extent.

The primary commercial advantage of mineral admixtures is to lower the amount of cement required to attain a given strength in the final structure. Adding a mineral admixture to a given cement mixture produces multiple effects: improved workability, retardation of set and reduced thermal cracking, increased ultimate strength, increased impermeability, and better durability to chemical attack such as by sulfate (Berry and Malhotra 1982).

The use of mineral additives has been studied as a method of reducing the general permeability of cured cement matrices containing low-level nuclear waste (Carlson 1987). Improved admixtures have exhibited markedly superior leach resistance, even for very mobile, radioactive cesium.

Soluble Silicate Admixtures

Soluble silicates have been added to waste S/S systems and were a part of an early patented process (Jones and Malone 1982). Recent studies (Davis et al. 1987) have confirmed the benefit of soluble silicate addition. These studies showed that added silicate levels up to 5 percent of the weight of the waste resulted in a 25- to 90-percent reduction in the metal ion concentration of an acid (pH 5) leachate. In S/S waste products including aggregates, the larger the aggregate, the larger the effect of added silicate.

Effects of soluble silicates have traditionally been credited to the formation of metal silicates that are more stable and less soluble than metal hydroxides (Falcone et al. 1984). However, data of Davis et al. (1987) using a simple penetration model suggested that the primary influence of the soluble silicate is due to a reduction in permeability and improved waste integrity. The soluble silicate apparently reacts with the free lime produced in the normal cement hydration process, decreasing the porosity and thus the permeability in a manner similar to the effects of added reactive silicates in fly ash or blast furnace slags, as discussed above.

POSSIBLE MECHANISMS OF THE EFFECTS OF ORGANIC COMPOUNDS ON PORTLAND CEMENT PRODUCTS

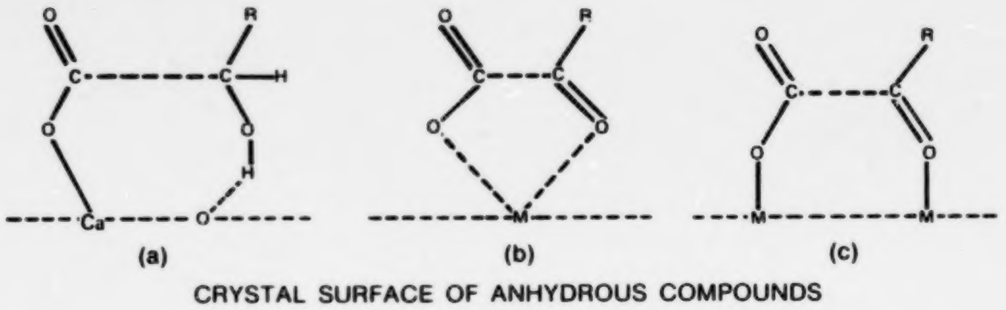
The variables associated with the use of admixtures in concrete production are numerous. These variables are magnified when a toxic waste is being considered for S/S. The variable and complex composition of a typical hazardous waste increases the complexity of evaluating the S/S process. The potential mechanisms for chemical influence of organic materials on Portland cement must be studied and understood. However, even then, the prediction of the effects of specific levels of individual waste constituents on final product characteristics will be difficult at best (Hansen 1959).

An example of the complexity surrounding the interaction of organics with cement matrices has been reported by Cartledge et al. (1987). Several phenols with different substituents on the aromatic ring were solidified with types I and III Portland cement at several concentrations up to 20 percent by weight of cement. At various times of cure, the products were extensively investigated using water and solvent extraction, optical and scanning electron microscopy, X-ray diffraction, and NMR spectroscopy. Although all phenol derivatives were readily leached from all specimens, significant differences in physical characteristics (such as setting times and compressive strengths), the morphology of the cement matrix, and the nature of the crystalline phases were observed. The authors state that even subtle differences in the structure of the organic may result in major differences in the nature of the cement-organic interaction.

Several conceptual models of the interference mechanisms of organics on cementitious and pozzolanic are addressed below. These potential mechanisms include interference via adsorption, complexation, precipitation, and nucleation (Young 1972, 1976).

Adsorption

One possible interfering mechanism is adsorption of added molecules onto the surface of the cement particles, thus blocking the normal hydration reactions. Studies by Young (1972) have shown that the retarding effect of organic compounds is related to the strength of their adsorption on metastable, hexagonal, calcium aluminate hydrates. In this way the organic compound is thought to inhibit crystal growth and conversion to C_3AH_6. The inhibiting effect roughly correlates with the number of hydroxyl (e.g., alcohols, glycerol, or sugars), carboxylic (e.g., acids, acetic acid, citric acid), and carbonyl (e.g., ketones, dimethyl ketone, methyl ethyl ketone) groups in the organic molecule. Hansen (1952, 1959) noted the effect of two particular families of organic compounds (lignosulfonic acid derivatives and hydroxylated carboxylic acids) on setting reactions. Lignosulfonates are strongly adsorbed onto C_3A (Kawoda and Nishiyama 1960, Blank et al. 1963). The adsorption of calcium lignosulfonate onto C_3A results in a relatively thick film or layer, which is indicative of a chemical reaction involving the organic and C_3A hydration production. Adsorption of the hydroxylated carboxylic acids, such as gluconate or oxalates, involves simultaneous Ca^{+2} ion adsorption to the carboxyl groups and adsorption of silicate ions by the hydroxyl groups (Figure 3a). Taplin (1962) found retarding effects from



(a) (b) (c)

CRYSTAL SURFACE OF ANHYDROUS COMPOUNDS

Figure 3. Possible adsorption mechanisms of organic admixtures onto surfaces. (Note: C, H, O, M, R = carbon, hydrogen and oxygen atoms, metal, ions, and rest of the molecule, respectively.) (Source: Hansen 1952.)

aliphatic and aromatic dicarboxylic acids (e.g., maleic acid). In alkaline solutions where maleic acid has no hydroxyl group for hydrogen bond adsorption, chelation may be the mechanism of set retardation (Figures 3b and 3c).

The overall retardation of hydration can be the result of an initial acceleration followed by retardation. This effect has been observed with C_3A in the presence of sugars and also for C_3S hydration in the presence of lignosulfonates (Seligmann and Greening 1964, Chatterji 1967, Daugherty and Kowalewski 1968). The organic compound, when adsorbed onto the cement clinker, first assists in hydration, and later retards hydration by adsorption onto the hydration product. These effects are altered by the presence of sulfate ions, which increases the formation of ettringite and lowers that of C_3AH_6 because the adsorption of calcium lignosulfonate or sugar onto C_3A is reduced. The morphology of ettringite can also be modified by the presence of sugars (Daugherty and Kowalewski 1968).

The adsorption of organic retarders by C_3S and C_2S in an aqueous solution is much weaker than adsorption by C_3A. However, the amount adsorbed (3 to 5 mg/g on C_3S and 1 to 2 mg/g on C_2S) is sufficient to form a multilayer film on the C_3S and C_2S. The occurrence of calcium ion concentrations in the aqueous solution (Figure 4) soon after the addition of retarders indicates that the retarding reaction is not with C_3S or C_2S, but rather with other hydration products. Strong retarders can extend indefinitely the hydration of C_3S. Addition of hydrated C_3S or calcium hydroxide can curtail the retarder effect and permit hydration.

Although data indicate the stronger adsorption of organic compounds by C_3S, the organic retarders act primarily by retarding the C_3S hydration. Therefore, most of the retarder is adsorbed by C_3A, but sufficient amounts must be present to be adsorbed by C_3S to actually retard the set. In some instances, differential adsorptive properties and hydration dynamics make it advantageous to delay addition of the retarding agent (Bruere 1963, 1966). When addition of the retarder is delayed, the adsorption of C_3A is reduced, and adsorption on C_3S in increased. The initial set is not hindered; however, the retardation effect on the final set is increased.

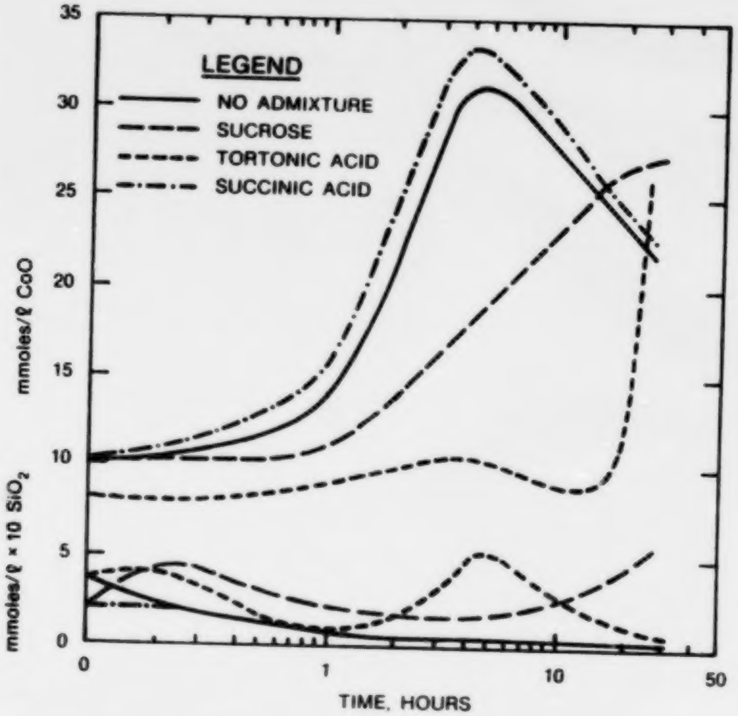


Figure 4. Influence of some organic admixtures on soluble CaO and SiO_2 during early hydration of tricalcium silicate. (1 wt % additions) (Source: Young 1972.)

Although adsorption of organic retarders is primarily on C_3A, retardation is due to adsorption on C_3S. There is no evidence of adsorption on C_3S. Nor is there evidence of adsorption onto anhydrous surfaces. Organic additives can have an important bearing on reaction rates during cement hydration. However, adsorption is not the only conceptual model that can account for set retardation.

Complexation

Taplin (1962) related the retarding activity of the organic compounds he studied to the proximity of oxygen atoms to carbon atoms. He observed that compounds with oxy-functional groups in proximity to each other were more effective as retarders. He theorized that chelation to metal ions was an important factor in set retardation. Calcium ions can chelate with various hydroxyl or carboxylic acids, but the retarder or accelerators (respectively) are so dilute that complexation of the calcium could not be an important factor (Young 1972).

The effects of complexing calcium are more significant when the additive to affected-ion ratio is large, and when the effected ion is important to the setting system. Such would be the case for the aluminate and ferrite ions.

Several workers (Kalousek et al. 1943, Suzuki and Nishi 1959, Roberts 1967) have shown that the addition of sucrose increases the concentration of alumina and calcium ions to above-normal levels. Experiments (Young 1972) with C_3A indicate that 1 wt % additions of sucrose, succinic acid, or tartaric acid increase the amounts of calcium and alumina in solution at first, but concentrations later decrease to normal or below normal. Silica concentrations are also increased when additives that affect alumina concentrations are used. Apparently, conditions in a cement paste are favorable for aluminate, ferrite, and silicate ion complexation. It is possible that complexation delays the formation of hydration products. When cement crystal-forming ions are kept in solution by complexation, hydration barriers are established that retard the set.

Precipitation

The formation of insoluble hydration products by additives reacting with cement compounds has been reported conceptually not to be a realistic mechanism of admixture interference (Young 1972). Certainly, the formation of insoluble compounds could impede water transport, solubility, and subsequent hydration reactions. However, if retardation is due to precipitation, then the process should be nonselective. In this case, C_3S and C_3A should both release calcium ions, and the resulting effect on setting should be equally weighted in regard to C_3S and C_3A activity. Regardless, the retardation is known to be related primarily to C_3A content (Young 1972).

However, if the precipitation reaction involves the hydration product itself, the precipitated product would preferentially be produced at the surface of the hydrating material. This is thought to be the mechanism of action of phosphates, borates, and oxalates (Mehta 1987).

Nucleation

The inhibition of nucleation of crystalline calcium hydroxide by soluble silica, which is present in small quantity, is believed to be the self-retarding set feature of C_3S hydration. Growth of a crystalline matrix is retarded by the adsorbed silica ions when a C-S-H layer results in a diffusion barrier to calcium hydroxide. Eventually, crystal growth results in the adsorbed silica being trapped in the crystalline matrix as the hydration process continues. Prismatic growth of calcium hydroxide results from differential adsorption of silica on calcium hydroxide crystal faces (Young 1972).

It is postulated that organic retarders act much the same as silica ions in being adsorbed onto the calcium hydroxide nuclei. However, as the name implies, organic retarders are much more effective in being adsorbed and more completely cover the crystal growth surfaces. This results in part from more retarders being solubilized. The resulting retardation of crystal growth results in more crystallite nuclei forming in the saturated solution. The net effect of crystal growth on these many nuclei is responsible for the acceleration of C_3S hydration following the retardation period (Young 1976). With about 1 percent of a strong retarding agent, C_3S hydration is completely inhibited. Additions of prehydrated C_3S can overcome the effect of the organic retarder, lending support to an adsorption/nucleation model.

SECTION 5

EFFECTS OF WASTES ON CEMENT/POZZOLAN PROCESSES

INTRODUCTION

Acids, salts, bases, and organic materials may be present in hazardous wastes singly and in combinations. As such, predicting their single and collective effect on the durability and containment of the typical cement and pozzolan S/S processes presents a difficult problem for process designers and regulatory agencies. Long-term effects are especially difficult to estimate because subtle differences in environmental parameters can have significant long-term consequences on the integrity of the S/S waste.

Early concerns about the effects of industrial wastes in the environment on concrete corrosion are described by Biczok (1967). He lists industrial wastes that are harmless to concrete and mortar products:

1. Brines containing bases but no sulfates.
2. Potassium permanganate, occurring at fermenting and purification installations.
3. Sodium carbonate (soda) and potassium carbonate (potash).
4. Bases (caustic lyes of potash and soda, lime and ammonia), provided their concentration is not excessively high.
5. Oxalic acid occurring at tanneries.
6. Mineral oils and petroleum products (benzene, kerosene, cut-back oil, naphtha, paraffin, tar), as long as these contain no acids that can continue to remain in the products after chemical treatment.

Industrial wastes deemed to be aggressive and detrimental to concrete and mortar products are

1. Water containing gypsum, e.g., that used for quenching coal slag.
2. Ammonia salts.
3. Hydrochloric acid, nitric acid, and sulfuric acid.
4. Chlorine and bromine.
5. Acetic acid.
6. Pure alcohol (in certain cases only, e.g., absolute alcohol, owing to the dehydrating effect).
7. All sulfur and magnesium salts.
8. Hydrogen sulfide and sulfur dioxide gas.
9. Animal fats.
10. Salts of strong acids, formed with magnesium, zinc, copper, iron, aluminum, and other metals, the hydroxides of which are poorly soluble in water.
11. Vegetable, animal, and some acidic.

Biczok (1967) also suggests that besides the wide variety of salts listed above, the salts formed by weak bases and strong acids, such as $ZnSO_4$, $ZnCl_2$,

$Zn(NO_3)_2$, $FeSO_4$, $FeCl_2$, $Fe(NO_3)_3$, $CuSO_4$, $CuCl_2$, $Cu(NO_3)_2$, $Al_2(SO_4)_3$, $AlCl_3$, and $Al(NO_3)_3$, may be regarded as potentially aggressive. Furthermore, chlorine, bromine, and iodine are considered to be aggressive. If sugar, molasses, spirit, ammoniac, salt, strong acids or animal fats are present, expert opinion based on literature information, practical experience, or previous analyses should be obtained.

ORGANIC WASTES

A few studies have been directed toward the effects of typical organic waste components upon cement and pozzolan S/S processes. However, most of these studies did not include extensive testing of the resultant S/S waste products. Strength and leaching tests are complicated by the fact that the setting waste/binder matrix is a dynamic system whose properties will vary considerably over the first few weeks or months after they are produced. For instance, many of the materials that retard the initial setting of cement and pozzolan products will result in higher ultimate strength and containment properties of the solid (see Roberts 1978 and Smith 1979). A further complication is that interference effects can vary with cement- or pozzolan-to-water ratio, interactions with other waste components, and even with order, type, and timing of mixing.

Portland Cement Mixtures

The mechanisms by which organic constituents interact with cement matrices is important to predicting the long-term effects of S/S waste technologies. Ideally, long-term stability could be assayed using short-term testing techniques. Several testing techniques such as X-ray diffraction and electron and optical microscopy are necessary to assess the effects of waste constituents on the complex chemistry of cement setting reactions (Tittlebaum et al. 1986). There is also some information that the chemical matrix of inorganic binders can increase the solubility and reactivity of organic waste components (Wiedemann 1982). Some organics have greater water solubility and reactivity in a strong acid environment, while others are more reactive under strong alkaline conditions. Phenols, for example, are transformed to more reactive phenolates in basic pHs. The water solubilities of some compounds like kepone also vary with pH.

Clark et al. (1982a,b) studied selected cement media to determine interference and retention capacities of an oil and a synthetic organic liquid mixture (see Table 13). Media used in the study included Portland type I cement, vermiculite plus Portland type I cement, Nutek 380-cement process (Nuclear Technology Corporation), Portland type I cement with sodium silicate and an oil emulsifier, Delaware Custom Materials' (DCM) cement process, and U.S. Gypsum's Envirostone Process. All of the processes were applied to stabilization of oil (Inland Vacuum Industries No. 19 Vacuum Pump Oil), but only the Nutek and Envirostone processes were applied to the synthetic organic liquid. The solidified waste forms were evaluated only in terms of being free-standing, monolithic solids and having no free liquids following solidification. Other preliminary testing was conducted only on selected specimens--immersion testing (72 hours soak to check for loss of integrity), vibratory shock testing, and flame testing. Approximately 100 subjectively determined formulations were prepared and examined.

TABLE 13. COMPOSITION OF SIMULATED ORGANIC LIQUID WASTE USED BY CLARK ET AL. (1982)

Component	Volume %	Component formula
Methanol	22	CH_3OH
Ethanol	22	C_2H_5OH
Acetone	9	CH_3COCH_3
Isopropanol	5	$CH_3CHOHCH_3$
Diethyl ether	9	$C_2H_5OC_2H_5$
Ethyl acetate	4	$C_2H_5COOCH_3$
n-Hexane	9	$CH_3(CH_2)_4CH_3$
Benzene	4	C_6H_6
Toluene	4	$C_6H_5CH_3$
Acetonitrile	4	CH_3CN
1,2-Ethylene dichloride	4	$C_2H_4Cl_2$
Chloroform	4	$CHCl_3$

In general, loadings of the oil up to 30 percent of the volume of final product yielded free-standing solids that passed the immersion test. However, loadings of over about 10 percent of the organic liquid waste cause loss of physical integrity and the formation of free liquid from the solidified product. The 10 formulations judged by Clark et al. (1982) to have the highest loadings and which gave satisfactory monoliths using their criteria (given only as "reasonable physical integrity") are given in Table 14.

Telles et al. (1984) presented a review of available treatment processes used in the S/S of organic wastes. Table 15 summarizes the organic contaminants reported and the S/S materials covered in their review. Telles et al. (1983) presented some unpublished results from studies involving fixation of synthetic sludges containing chromium, cadmium, lead, and nitrocellulose. The fixatives were polysilicates and amine-cured epoxides. Inorganic dry sludge containing Pb, Cr, and Cd was treated with polysilicates and with polysilicates in combination with Portland cement and fly ash. An organic wet sludge containing nitrocellulose was also treated with polysilicates. The fixing agents were mixed in five compositions that included variable amounts of the following: sodium silicate, Portland cement, fly ash, $CaCl_2$, HNO_3, and NaOH. The mixtures of the various compositions were allowed to cure from 3 to 4 days and then were subjected to extraction procedure (EP) toxicity testing to determine the effectiveness of the fixation mechanism in regard to leaching of contaminants.

TABLE 14. FORMULATIONS JUDGED TO YIELD THE MOST SATISFACTORY SOLIDS

Formulation (wt %)				Organic loading (vol %)	% Loss of water on curing
Immobilization media		Water	Organic		
30	Portland cement (I)	60	5 Oil	12	2
55	Portland cement (I)	28	17 Oil & vermiculite (50% saturated)	11	13
55	Portland cement (I)	25	20 Oil & vermiculite (100% saturated)	30	10
44 1.9 2.9 6	Portland cement (I) & Nutek 380A Nutek 380B Lime	8.8	19 Oil	29	NA*
53 20 3	Portland cement (I) & Nutek 380A Nutek 380B	4.6	20 Oil	30	NA
58 6.3 1.1	Portland cement (I) & Nutek 380A Nutek 380B	21	6.1 Organic liquid	9	NA
46 2 3.8	Portland cement (I) & Emulsifier Sodium silicate	25	23 Oil	39	NA
51 1.6 2.8	DCM Cement & Emulsifier Sodium silicate	27	17 Oil	30	NA
52 2.2	Envirostone cement & Emulsifier	26	24 Oil	36	21
50 6.5	Envirostone cement Emulsifier	35	8.1 Organic liquid	11	NA

Source: Clark et al. 1982.
* NA = not analyzed.

TABLE 15. ORGANIC CONTAMINANTS AND FIXATIVES USED IN EXPERIMENTAL STUDIES

Contaminants	Fixatives
PCBs	Cement-based processes/silicates, polyesters, limes, polymer-cements
Kepone	Cement-based/silicates, sulfur, epoxide
Various chlorinated aliphatic and aromatic hydrocarbons	Cement-based/proprietary organic polymers, gypsum
Phenol, toluene	Cement-based/silicates
Ion-exchange resins	Cement-based/silicates, polymer-cements, epoxides, polyester, asphalt, polyethylene gypsum, ureas
Various pesticides	Polymer-cements, polybutadiene/polyethylene (surface encapsulation)
Oils	Cement-based/silicates, polymer cements, proprietary polymers, ureas
Mixed solvents*	Gypsum, polymer-cements, cement/silicates
Nitrocellulose	Cement/silicate, epoxide
Dioxin	Calcium oxide, asphalt, Portland cement, asphalt/sulfur

Source: Telles et al. 1984.

* A mixture comprised of the following: alcohols, ketones, aldehydes, esters, ethers, alkanes, acetonitrite, and chlorinated cleaning solvents.

Acceptable leaching performance for calcium-polysilicate fixed contaminants was only obtained in these tests at or below the 0.2-percent weight (2,000 ppm) loading of Pb. Mixtures with Cd, Cr, and Pb were also managed at the 0.2-percent weight loading. Results of tests on contaminants fixed with sodium silicate and Portland cement indicated that samples with contaminant loadings as high as 24,000 ppm (2.4 percent) were able to meet EPA toxicity criteria. Organic sludges containing nitrocellulose were not acceptably stabilized using polysilicates and Portland cement.

Buchler (1987) studied the adsorption of water-soluble organic molecules onto a tetramethyl ammonium chloride (TAC) derivative of Wyoming bentonite clay as a possible S/S pretreatment method. The hydrophobic nature of the TAC compared with the normal sodium cation makes the clay more receptive to organic molecules, especially polar organics. The strength of the adsorption was inversely proportional to the temperature so that higher leaching losses would be expected in the summer months. Treatment of 1,000-ppm phenol wastes at 20° C produced an effluent containing 150 ppm phenol; effectiveness decreased at lower phenol concentrations and higher temperatures. Glucose, glycine, and dextran were also tested but showed a lower adsorption pattern.

In a similar study, Sheriff et al. (1987) used activated charcoal as well as tetra-alkylammonium substituted bentonite clays as prestabilization adsorbents before incorporating them in a number of cementitious matrices. They found a clear trend between the degree of polarity of substituted phenols and their ability to be absorbed by the substituted clays. Activated charcoal effectively adsorbed up to a 1,000-ppm concentration of the phenols and chlorinated phenols. Leachability and physical strength measurements are to be carried out on the S/S products.

Newton (1987) described an organic S/S system in which a fast sorption interaction occurs between a sodium magnesium fluorolithosilicate and/or sodium bentonite that has been reacted with a quaternary ammonium compound. Other admixtures are also added to decrease the permeability of the final product and to improve mixing and leaching characteristics. The formulation is being sold as a proprietary S/S agent that is claimed to have been successful in treating a variety of organic-bearing wastes.

An amorphous silicate glass foam of 8 to 200 mesh spheres with numerous cells has been suggested to be the universal sorbent material (Temple et al. 1978). The material is free-flowing granules with a loose bulk density of 2 lb/cu ft (32 kg/cu m). The material is said to be an excellent absorbent for acid, alkalies, alcohols, aldehydes, arsenates, ketones, petroleum products, and chlorinated solvents. It absorbs more than 10 times as much liquid as expanded clays, and its sorbent capacity ranges from 0.77 gal/lb (6.4 cu dm/kg) for perchloroethylene to 1.82 gal/lb (15 cu dm/kg) for phosphoric acid. The loaded material has safely been solidified using Portland cement and sodium silicate, but no testing results were available.

Roberts (1978) and Smith (1979) report results of an extensive study of the effects of selected organics upon the strength and leaching characteristics of a typical lime/fly ash S/S formulation. Organic compounds included methanol, xylene, benzene, adipic acid, and an oil and grease mixture.

The effects of ethylene glycol on cement-based solidification processes have been documented (Chalasani et al. 1986, Walsh et al. 1986). These investigators used a combination of techniques including extraction with solvents of varying polarity, scanning electron microscopy, and X-ray powder diffraction. The ethylene glycol appears to occupy three different sites in the solidified product as ascertained by their different extractability. No visible gross alteration in morphology of the cement matrix is apparent until the ethylene glycol reaches around 10 percent of the cement by weight. Levels above 10 percent clearly weaken the structure and cause higher leachability of the compound. Some evidence from X-ray diffraction indicates that the ethylene glycol moves into the 0.5- to 2.5-nm voids in the C-S-H gel phase and alters its structure. A major effect of the organic addition is the retardation of setting reactions so that significant changes in the matrix occur for up to at least 1 year of curing time.

Conner (1984) describes the successful solidification of 4 million gallons of waste containing 6.6 percent ethylene glycol, 2.5 percent sodium terephthalate, 8.3 percent sodium chloride, and 234 mg/ℓ antimony. The final product had a UCS of 55 to 70 psi (0.38 to 0.48 MPa) and leached 0.1 mg/ℓ antimony, 5 mg/ℓ sulfate, 160 mg/ℓ chloride, and 350 mg/ℓ chemical oxygen demand. No details on the type of reagents or leaching tests used were given.

Gilliam et al. (1986) studied the immobilization of four waste streams in simple cement grout. One of the wastes contained 2,230 ppm PCBs and 17,400 ppm each of lindane (hexachlorocyclohexane), pentachlorophenol, and 9,9'-dichlorofluorene (PNA) dissolved in a typical pump oil. The waste was solidified using 19 wt percent Portland cement (type I), 17.5 percent fly ash (class F), 37.7 percent water, 3 percent attagel 150, 1.7 percent microcel E, 0.1 percent Sparr 80 emulsifier, and 0.02 percent Tributyl PO_4 antifoam so that a total waste loading was 20 percent by weight. Leaching of the solid after 90-day cure in 100-percent humidity using the MCC-1 static leaching procedure (Materials Characterization Center 1981) gave saturation values after 28 days of leaching of <1.5 ppb PCBs, <0.76 ppb lindane, less than 10 ppm pentachlorophenol, and 0.607 ppm dichlorofluorene. The authors state that by tailoring and adjusting the mixture, satisfactory solidification of organic wastes in these categories (PCBs, chlorinated cyclohexane, chlorinated phenol, and PNAs) should be possible.

Pozzolanic Systems

Limited information is available on the effects of organics in pozzolanic systems. Researchers have suggested that unpyrolized organics reduce the cementing ability of fly ash by taking up reactive surface sites of the ash and preventing cementing-type contact of the various constituents (Davidson et al. 1958, Leonard and Davidson 1959, Thorne and Watt 1965, Thornton et al. 1975). Thornton et al. (1975), however, did show that pozzolans could be used to solidify clay soil with an organic content of 11.4 percent. The addition of a 5-percent lignite fly ash to the soil increased the UCS approximately 40 percent.

The compounds were added up to 8.5 percent of the dry weight of the reagents; the formulations used are shown in Table 16. The organics range in water solubility from very high to virtual insolubility and cover a structural range from simple single carbon alcohol to linear organic acids, to simple and substituted aromatic ring, to long unsaturated hydrocarbon chains.

Unconfined compressive strengths were made on 40-gram minicylinders (1 in. diameter by 2 in. height) that were prepared on a Carver hydraulic press (500 psi (3.4 MPa) for 20 sec). During compaction, all 8.5-percent organic mixes exuded some of the organic material. Only the adipic acid at both 1- and 8.5-percent formulations appreciably affected the compressive strength after 2 or 3 months. Adipic acid is a 6-carbon, dicarboxylic acid that must neutralize the added lime (producing calcium adipate) and therefore interfere with the pozzolanic reaction. Also evident is the action of methanol as a retarder of the pozzolan reaction. But typical of most retarders, the ultimate strength of the mixture eventually equals that attained by the control. Such a delay in setting time is not generally considered to be important in most waste S/S processes. Smaller delays in setting time are also evident for xylene and benzene at 8.5 percent, the effect of benzene still evident (but not significant) after 90 days of cure.

TABLE 16. EFFECTS OF SELECTED ORGANICS ON UCS AND LEACHING CHARACTERISTICS OF A LIME/FLY ASH FORMULATION

Formulations* % dry weight			Unconfined compressive strength† (days curing @ 23° C)					Leaching test results‡							
								28-day cure				90-day cure			
Fly ash	Lime	Additives	7	14	28	62	92	pH	Ca	TDS	TOC	pH	Ca	TDS	TOC
95.2	4.8	None	190	315	454	579	664	11.65	225	890	29	11.40	81	728	8
95.1	4.8	0.1 Methanol	223	305	371	495	570	11.70	215	836	40	11.15	71	714	10
94.2	4.8	1.0 Methanol	219	301	435	542	618	11.55	140	564	173	11.35	63	712	87
87.1	4.4	8.5 Methanol	37	41	200	510	648	11.90	480	1046	1538	11.40	100	762	734
95.1	4.8	0.1 Xylene	257	310	446	557	666	11.70	210	746	40	11.40	71	724	10
94.2	4.8	1.0 Xylene	247	308	421	535	655	11.70	205	726	44	11.45	63	652	27
87.1	4.4	8.5 Xylene	201	297	362	497	640	11.85	355	900	62	ND	ND	ND	ND
95.1	4.8	0.1 Benzene	246	313	435	525	637	11.65	150	606	29	11.40	63	706	10
94.2	4.8	1.0 Benzene	245	301	452	540	621	11.70	205	768	39	11.40	81	626	9
87.1	4.4	8.5 Benzene	196	267	317	415	553	11.90	410	1030	41	ND	ND	ND	ND
95.2	4.8	None	185	279	290	426	401	ND	ND	ND	ND	12.30	ND	ND	ND
94.2	4.8	1.0 Adipic acid	62	95	117	218	187	ND	ND	ND	ND	12.10	ND	ND	ND
87.1	4.4	8.5 Adipic acid	57	69	66	70	77	ND	ND	ND	ND	10.20	ND	ND	ND
94.3	4.8	1.0 Oil & grease	165	271	351	515	485	ND	ND	ND	ND	12.10	ND	ND	ND
87.1	4.4	8.5 Oil & grease	161	314	388	466	488	ND	ND	ND	ND	12.10	ND	ND	ND

Source: Roberts 1978, Smith 1979.

Note: ND = no data; TDS = total dissolved solids; and TOC = total organic carbon.

* All mixes prepared at 82-percent solids (including organics).

† All values given in pounds (force) per square inch and are an average of three determinations. (To convert values to megapascals, multiply by 0.00089457.)

‡ All values (except pH) are in milligrams per litre of leachate (from ASTM 48-hour leaching test).

Selected leaching results upon the minicylinders after 28 and 90 days are also shown in Table 16. The pH, total dissolved solids (TDS), calcium (Ca) and total organic carbon (TOC) content of the leachates increased in the 8.5-percent mixes of methanol, xylene, and benzene in the 28-day cure test. Although not shown in Table 16, the loss of methanol is quite high from the 8.5 percent mixes and remains so after 90 days of curing; these losses represent about 20 percent of the added methanol in 48 hours of leaching from the samples cured 28 days and about 10 percent after 90 days of curing. The general tendency toward reduced loss for all constituents is evident for all parameters analyzed.

No significant effect of the addition of methanol, xylene, or benzene is seen for either arsenic or chromium (data not shown). In all cases, arsenic averaged around 0.01 mg/ℓ in the leachates from both the 28- and 90-day cured samples. Chromium averaged around 0.06 mg/ℓ in the 28-day cure samples and 0.10 mg/ℓ after 90 days cure.

The X-ray diffraction analysis of all of the formulations gave little information except that no new crystalline compounds were formed in detectable amounts. Scanning electron micrographs indicated that the presence of the organic compounds altered the morphological structure of the lime/fly ash reaction products, even at the 0.1-percent level and even though compressive strength and leaching character were not affected appreciably.

Smith (1979) concluded that a good correlation exists between his findings for the effects of organic compounds on lime/fly ash pozzolanic systems and reported effects on the hydration of Portland cement; therefore, the large amount of information concerning additives and inferences on Portland cement should also be applicable to systems using pozzolanic reactions. Some organic wastes appear to be compatible with these systems, such as rolling mill sludges, electroplating wastes, or oily sludges from petroleum refineries. However, organic wastes containing hydroxyl or carboxylic acid functional groups, such as biological wastes, paint sludges, and some solvents, can be expected to delay or completely inhibit the pozzolanic reactions responsible for solidification.

Summary of Organic Effects

In a recent study, Spooner et al. (1984) reviewed existing information about the capability of S/S binders with different classes of organic chemicals. Material for this study was obtained through a literature review and through contacts with representatives from universities, industry, trade associations and government agencies. From the gathered information, matrices were developed which summarized and defined the compatibilities of various S/S binder systems with particular chemical groups.

The binder categories chosen for Spooner's study include: Portland cement types I, II, and V; clay (bentonite); clay-cement; and silicates. The chemical categories chosen were divided into 16 groups that represented the types of organic compounds most likely to be found in hazardous wastes and in leachate from a hazardous waste disposal site. Table 17 (Spooner et al. 1984) was developed from the data gathered. It presents a matrix of information

TABLE 17. DOCUMENTED INTERACTIONS BETWEEN S/S BINDERS AND SPECIFIC CHEMICAL GROUPS

Chemical group	Portland cement				
	Type I	Types II & V	Bentonite	Clay-cement	Silicate
Organic Compounds					
Alcohols & glycols	Durability: decrease (destructive action occurs over a long time period)	Durability: decrease (destructive action occurs over a long time period)	Durability: decrease (destructive action occurs over a long time period)	Durability: decrease (destructive action occurs over a long time period)	D/U
Aldehydes & ketones	D/U	D/U	Durability: decrease (destructive action occurs over a long time period)	D/U	D/U
Aliphatic & aromatic hydrocarbons	Set time: increase (lengthen or prevent from setting) Durability: no significant effect	Set time: increase (lengthen or prevent from setting)	Durability: decrease (destructive action occurs over a long time period)	D/U	D/U
Amides & amines	D/U	D/U	D/U	D/U	D/U
Chlorinated hydrocarbons	Set time: increase (lengthen or prevent from setting) Durability: decrease (destructive action occurs over a long time period)	Set time: increase (lengthen or prevent from setting) Durability: decrease (destructive action occurs over a long time period)	D/U	D/U	D/U

(Continued)

Source: Spooner et al. 1984.
Note: D/U = data unavailable.

TABLE 17. (Concluded)

Chemical group	Portland cement			Clay-cement	Silicate
	Type I	Types II & V	Bentonite		
Ethers & epoxides	D/U	D/U	D/U	D/U	D/U
Heterocyclics	D/U	D/U	Durability: decrease (destructive action occurs over a long time period)	D/U	D/U
Organic Compounds					
Nitriles	D/U	D/U	D/U	D/U	D/U
Organic acids & acid chlorides	Set time: no significant effect Durability: decrease (destructive action occurs over a long time period)	Set time: no significant effect Durability: decrease (destructive action occurs over a long time period)	Durability: decrease (destructive action occurs over a long time period)	Durability: decrease (destructive action occurs over a long time period)	Durability: no significant effect
Organometallics	D/U	D/U	D/U	D/U	D/U
Phenols	Set time: no significant effect Durability: decrease (destructive action occurs over a long period)	D/U	Durability: decrease (destructive action occurs over a long time period)	Durability: decrease (destructive action occurs over a long time period)	D/U
Organic esters	D/U	D/U	D/U	D/U	Set time: no significant effect

concerning the effects of different chemical groups upon selected binder types in terms of effects on set time and durability.

The isolation of hazardous organic wastes by solidification with cementitious and pozzolanic materials appears to have good potential to be economical and effective. However, additional study is needed on individual waste and S/S process combinations before long-term stability can effectively be predicted. Rapid progress should be made by the application of existing knowledge of cement and pozzolan chemistry and the effects of admixtures and impurities upon them.

INORGANIC WASTES

Shively et al. (1986) made up cement paste samples with each of four hazardous waste constituents (arsenate, calcium, chromium, and lead) and another sample with a mixture of the four. Unconfined compressive strengths (14-day) and leaching characteristics of the wastes were examined. The UCS values are shown in Table 18. Sodium arsenate and cadmium nitrate reduced the 14-day strength at both water-cement (W/C) ratios. The lead nitrate retarded the setting time by several hours, but neither the lead nitrate nor the chromium chloride affected 14-day strength at either W/C ratio. The arsenate sample set within 15 minutes of mixing, which was much faster than the other samples. Although the setting time was not noticeably different for the cadmium samples, the authors speculate that the chemical association of arsenate and cadmium in the cement paste may have interfered with the formation of the cement matrix compounds (C-S-H), resulting in the reduced strength.

Arlinguie et al. (1982) examined the effect of zinc on the hydration of C_3S and C_3A, the two principal Portland cement components, using X-ray diffraction. The hydration of C_3S was retarded to a greater degree than that of C_3A and appeared to be more important to the effect of zinc on hydrating cement pastes. Arlinguie et al. (1982) found that the retardation was due to the precipitation of an amorphous layer of zinc hydroxide around the anhydrous C_3S grains. The effect of the coating depended upon its low permeability. The hydration reaction began to occur more rapidly after the zinc hydroxide was transformed into crystalline calcium zinc hydroxide ($CaZn_2(OH)_6 \cdot 2H_2O$), which again allowed water to reach the surface of the cement grains.

Spooner et al. (1984) have also summarized the known effects of inorganics on S/S binder systems (Table 19). Although their categories are very broad, the fact that inorganics have pronounced effects on set time and durability of the final product is well illustrated by the table.

TABLE 18. UNCONFINED COMPRESSIVE STRENGTHS OF WASTE MIXTURES

S/S waste type	Concentration in waste (molarity)	14-day UCS (psi)	
		33% waste	50% waste
Control	———	4,830	1,520
Arsenate	2.4% (0.32)	3,020*	371*
Cadmium	2.3% (0.20)	2,960*	870*
Chromium	2.4% (0.46)	5,060	1,570
Lead	2.3% (0.11)	3,970	1,420
Mixed	0.2% As; 0.45 Cd 0.208 Cr; 0.83 Pb (all 0.04 molar)	3,920*	2,040

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* Significantly different from blank at 99-percent confidence level.

TABLE 19. DOCUMENTED INTERACTIONS BETWEEN S/S BINDERS AND SPECIFIC INORGANIC CHEMICAL GROUPS

Chemical group	Portland cement		Bentonite	Clay-cement
	Type I	Types II & V		
Heavy metal salts & complexes	Set time: increase (lengthen or prevent from setting) Durability: decrease (destructive action begins within a short time period)	Set time: increase (lengthen or prevent from setting) Durability: no significant effect	Durability: decrease (destructive action occurs over a long time period)	Set time: increase (lengthen or prevent from setting) Durability: decrease (destructive action begins within a short time period)
Inorganic acids	Set time: no significant effect Durability: decrease (destructive action occurs over a long time period)	Set time: no significant effect Durability: no significant effect	Durability: decrease (destructive action begins within a short time period) For modified bentonites Durability: decrease (destructive action occurs over a long time period)	Durability: decrease (destructive action begins within a short time period)
Inorganic bases	Set time: no significant effect Durability: no significant effect	Set time: no significant effect Durability: no significant effect Except KOH & NAOH - Set time: no significant effect Durability: decrease (destructive action occurs over a long time period)	Durability: decrease (destructive action begins within a short time period) For modified bentonites - Durability: decrease (destructive action occurs over a long time period)	Durability: decrease (destructive action occurs over a long time period)

(Continued)

Source: Spooner et al. 1984.

TABLE 19. (Concluded)

Chemical group	Portland cement		Bentonite	Clay-cement
	Type I	Types II & V		
Inorganic salts	Set time: increase (lengthen or prevent from setting) Durability: decrease (destructive action begins within a short time period)	Set time: increase (lengthen or prevent from setting) Durability: no significant effect	Set time: increase (lengthen or prevent from setting) Durability: decrease (destructive action occurs over a long time period)	Durability: decrease (destructive action occurs over a long time period) Except sulfates - Durability: decrease (destructive action begins within a short time period)

SECTION 6

ASPHALTIC AND POLYMERIC BINDERS

ASPHALT

Asphalt and bitumens are often suggested as S/S agents for low-level radioactive and soluble hazardous wastes. Bituminous materials, since they are not immiscible in water and are quite stable, will effectively isolate soluble components from contact by water for long periods of time (Thompson et al. 1979). Major drawbacks of the asphaltic S/S process for common, toxic wastes are its flammability, the need to mix at high temperature, and the cost of the raw material and mixing equipment. A summary of common types of asphalt as given as Table 20. The information most pertinent in intermixing waste and asphalt is the viscosity properties and flash point of the asphalt.

Asphalt is a dark-brown to black cementitious material, solid or semisolid in consistency, in which the predominating constituents are bitumens, which occur in nature or are obtained as the nonvolatile solids in petroleum refining. It is a mixture of paraffinic and aromatic hydrocarbons and heterocyclic compounds containing sulfur, nitrogen, and oxygen.

Considerable work has been undertaken by the Werner-Pflerderer Corporation, Waldwick, NJ, on the use of their extruder-evaporator to mix hazardous wastes with asphalt for S/S (Doyle 1979). A volume reduction and solidification system utilizing an extruder-evaporator was developed to meet the need for a process to handle a variety of chemical properties associated with the relatively low-volume, highly toxic wastes, such as arsenic, heavy metals, or electroplating-type wastes. The system, designed to process liquid and solid wastes generated from industrial processes, produces a solidified end product with the hazardous constituents, regardless of their chemical characteristics, immobilized in an asphaltic binder. It can handle a wide variety of liquid and dry waste feed streams, in conjunction with most plastic binders (asphalt, polyethylene, polypropylene, urea formaldehyde, and vinyl polyesters). The extruded-evaporator, in one step, evaporates all unwanted water or other solvent from the waste while homogenizing the waste constituents with the liquid plastic binder for discharge into a container. Once this waste-plastic mix has cooled, a significant volume reduction is realized.

As with cement and pozzolan, some information is available from the construction uses of asphalt, which deal with the effects of additives and impurities upon its final strength and properties. The effect of selected chemical additives in low concentration (less than 1 percent by weight) on the stabilization of fine-grained soil (a clayey silt from Massachusetts) with asphalt was studied by Michaels and Puzinauskas (1956, 1958). Soil samples were stabilized with either asphalt-gasoline cutbacks or asphalt-in-water emulsions, and the chemical additives examined were either incorporated with the asphalt or used to pretreat the soil before asphalt addition. Properties of the stabilized soil examined were primarily UCS after curing and

TABLE 20. COMMON ASPHALT TYPES

Type	Viscosity range	Uses	Pure asphalt %	Use Temp. °C	ASTM minimum flash point* °C
Blown asphalt (oxidized) ASTM D312	---	Steep roofing, pipe coating under sealing, cavity filling waterproofing	100	135° (min.)	225° (min.)
Asphalt cement ASTM D946, D3381 penetration & viscosity graded	80-550 centistokes† at 135° C	Plant-made asphalt concrete for roads, sidewalks, parking lots, dam facings, penetration macadam.	100	82°-176°	163°-238° (min.)
Cutback asphalt rapid, medium, or slow curing, ASTM D2028, D2027, D2026	30-6000 centistokes at 60° C	Road mixing of asphalt concretes. Asphalt penetration applications. Prime & tack coats before paving. Stock-piled patching mixes.	50-80	57°-116°‡	RC-27° MC-38°-66° SC-66°-107°
Emulsified asphalts, rapid, medium, or slow setting, ASTM D977, D2397	20-100 Saybolt Seconds at 25° C	Seal coating, penetration macadam, road mixing of asphalt concretes. Fine aggregate or soil stabilization. Cold or hot plant mixing. Patching mixes.	55-65	10°-71°	Will not flash

Source: Triegel et al. 1984.

* Flash points of specific products may exceed the minimum required by ASTM for that category.

† To convert centistokes to square metres per second, multiply by 0.000001.

‡ Application temperature may exceed flash point. Caution must be exercised.

compressive strength and water absorption after water immersion. It was found that addition of phosphorous pentoxide, benzene phosphoric acid, certain epoxy resins, and certain organic isocyanates to asphalt cutback significantly improved the strength characteristics of asphalt-stabilized soil. Addition of antistripping additives to asphalt cutback generally reduced strength and increased water absorption, but pretreatment of soil with such additives before incorporation of asphalt cutback was found to have a beneficial effect on strength and water resistance.

Soils stabilized with asphalt emulsions containing soap as the emulsifier were found to have strengths less than dry cutback-stabilized soil. On the other hand, soil stabilized with emulsions containing antistripping additives as emulsifiers exhibited wet strengths comparable to and, in some instances, superior to those stabilized with cutback. Mixing water-content and type of emulsifier appear to be major factors affecting stabilization. The authors concluded that chemical additives hold considerable promise in asphalt stabilization practices, offering opportunities for broader and more effective use of asphalt.

Asphalt has been used primarily for waste processing in the nuclear industry (Telles et al. 1984). Various other processes have also been investigated on a more limited basis. Asphalt fixation has been studied with hazardous wastes containing heavy metal salts (Kulkarni and Rosencrance 1983) and in encapsulation of trinitrotoluene waste sludges (Triegel et al. 1984).

Kobran and Guarini (1987) describe testing undertaken to prove conformance of WasteChem Corporation's Volume Reduction and Solidification (VSR) with the Nuclear Regulatory Commission's "Licensing Requirements for Land Disposal of Radioactive Waste" (10 CFR 61). Generic asphalt-encapsulated waste forms were tested, including bead resins, precoat filter cakes, evaporator concentrates, and decontaminated wastes. All samples were formed using high-viscosity, oxidized asphalt conforming to ASTM-D-312, Type III requirements. Maximum waste loadings were not given. Recommended compliance criteria and the results of the compliance testing are given in Table 21.

Mattus et al. (1987) report the results of the extensive testing of molded samples of an air-blown, ASTM type 3 bitumen with eight waste loadings. An aqueous waste containing 26 percent (weight basis) sodium nitrate and eight heavy metals and cesium and strontium was introduced directly into a continuous extruder. Test results include the 90-day ANS 16.1 Leach Test (American Nuclear Society (ANS) 1986), the U.S. EPA Extraction Procedure Toxicity Test, and unconfined compressive strength at all loadings. Also conducted were thermal differential and gravimetric scans, sizing of the fixed salts, flash and ignition point testing, and scanning electron microscopy of changes in surface morphology.

Telles et al. (1984) has indicated that with wastes having high contaminant loadings (>30 percent by weight) or for organics with low molecular weights, high vapor pressures, or hygroscopic natures, asphalt materials yield unacceptable fixation products. Sludges containing strong oxidizers such as nitrates, chlorates, perchlorates, and persulfates will react and cause a slow deterioration of the asphalt. Borates also present a problem in that they cause early hardening of asphalt materials much like a

TABLE 21. RESULTS OF COMPLIANCE TESTING ON WASTE LOADINGS

Test	Recommended acceptance criterion	Test results
Compressive strength	≥50 psi at 10% deformation	>50 psi at 10% deformation for all waste forms
Radiation stability	≥50 psi at 10% deformation after 10 rad exposure	>50 psi at 10% deformation for all waste forms after 10 rad exposure
Leach resistance	Leach index 6	Leach index >8 for all waste forms for Co, Sr, and Cs
Immersion	≥50 psi at 10% deformation after 90-day water immersion	>50 psi at 10% deformation for all waste forms
Thermal stability	≥50 psi at 10% deformation after 30 thermal cycles	>50 psi at 10% deformation after 30 thermal cycles for all waste forms estimated from short-term tests
Biodegradation for all waste forms in Hanford soil	Less than 10 weight percent degradation in 300 years	Less than 5.49 weight percent degradation in 300 years for all waste forms
Biodegradation for all waste forms in Barnwell soil	Less than 10 weight percent degradation in 300 years	Less than 4.57 weight percent degradation in 300 years for all waste forms estimated from short-term tests

Source: Kobran and Guarini 1987.

"quick set" in concrete processes. A summary of estimated compatibility of bitumen with various waste types is given in Table 22.

POLYMERIC AND OTHER THERMOPLASTIC BINDERS

Use of these types of S/S binders for waste treatment has been discussed for some time (Malone and Jones 1979), but only a few studies have been conducted on them. In general, the cost of the reagents and specialized equipment necessary has rendered them economically unfeasible. But some studies have looked at other binders for special problem wastes.

A process has been developed by Heiser et al. (1987) for the bench-top scale solidification of nitrate salt wastes in polyethylene. This study applies a methodology of polyethylene property, waste type selection, and waste form testing to identify and demonstrate the feasibility of the process.

TABLE 22. CHEMICAL COMPATIBILITY OF WASTES WITH BITUMEN

Waste type	Compatibility with bitumen
Ion exchange resins	Fair
Sludges	Good*
Boric acid wastes	Good
Sulfate wastes	Fair
Nitrate wastes	Poor
Phosphate wastes	Good
Carbonate wastes	Good
Oils	Poor-fair
Organic liquids	Poor-fair
Acidic wastes	Fair
Alkaline wastes	Fair
Filter cartridges	†
Large items	†

Source: Fuhrmann et al. 1981.
* Caution required with oxidizing sludges.
† Processes generally not applicable to these wastes.

The process uses a commercially available single-screw extruder that continuously discharges a prescribed polyethylene-waste mixture from the hoppers to the output die, where it is extruded into a container while still in the molten form. The molten mixture (110° to 120° C) conforms to the shape of the container and solidifies upon cooling. Proportional feeders serve to maintain quality control and homogeneity of the waste form over a wide range of waste/binder ratios. Present studies use dry wastes resulting from advanced volume-reduction technologies, although wet solid wastes can be processed using vented extruders of the type used for the bitumen solidification process. The simplicity of the system results in reproducible, homogenous waste forms.

Property evaluation tests were performed to determine leachability and mechanical stability. Emphasis is placed upon leaching of nitrates from the waste forms. Leach tests were performed according to EPA Extraction Procedure as well as ANS 16.1. For polyethylene waste forms containing 30 to 70 wt % sodium nitrate, ANS 16.1 leach indices range from 11 to 7.8.

Differential scanning calorimetry (DSC) was used to confirm the compatibility of the polyethylene and simulated salt waste, since some waste streams contain strong oxidizers. Components of the polyethylene/$NaNO_3$ system alone and in combinations were tested by DSC to detect chemical interactions at elevated temperatures (up to 400° C). No chemical reactions were discernible even above the decomposition temperatures of the nitrate salts.

Another organic binder being tested for nuclear wastes is Dow vinyl ester-styrene (Rogers and McConnell 1987). Vinyl ester-styrene is a thermosetting resin marketed by Dow Chemical Company for the S/S of radioactive waste. The resin is mixed directly with either wet solid wastes or dry wastes and subsequently polymerized at room temperature using a promoter-catalyst system. Wet wastes and the resin are emulsified using a high-shear mixing prior to initiating the polymerization reaction. The polymerization reaction is exothermic, and a monolithic solid is produced in 30 to 60 minutes.

SUMMARY

Spooner et al. (1984) have searched the literature extensively to assess documented reports of the effects of organic and inorganic chemicals on several types of chemical grouts and binder systems. These are summarized in Tables 23-25.

Spooner et al. (1984) have also developed a matrix that contains predictions or estimates of binder/chemical interactions for organic chemical groups (Tables 26 and 27) and for inorganic compounds (Tables 28 and 29). These compatibility predictions are based on the chemical structure, reaction theory, and estimated behavior of binders in the presence of the various chemical groups. The following assumptions were used in making the predictions given in Tables 28 and 29:

1. Typical landfill leachate has a high salt content, approximately 1 percent organic compounds concentration, less than 1 percent metal ions concentration, and a pH between 3 and 11.

2. Groundwater flow is nonturbulent and is a multicomponent dilute solution in which interactions between components do not occur; interactions may occur between these components and the binder, however.

3. Complete reactions between organic polymer binders and their curing agents do not occur, and other unreacted constituents will remain.

TABLE 23. DOCUMENTED INTERACTIONS BETWEEN ORGANIC S/S BINDERS AND SPECIFIC CHEMICAL GROUPS

Chemical group	Bitumen	Acrylamide
Organic compounds		
Alcohols & glycols	Durability: No significant effect	Durability: decrease
Aldehydes & ketones	Durability: decrease (destructive action occurs over a long time period) Aldehydes only - Set time & durability: no significant effect	Durability: no significant effect
Aliphatic & aromatic hydrocarbons	Durability: decrease (destructive action occurs over a long time period)	Durability: no significant effect
Amides & amines	D/U	D/U
Chlorinated hydrocarbons	D/U	Durability: no significant effect
Ethers & epoxides	D/U	Durability: no significant effect
Heterocyclics	D/U	Durability: no significant effect
Nitriles	D/U	D/U
Organic acids & acid chlorides	Durability: no significant effect	Set time: increase (lengthen or prevent from setting) Durability: no significant effect
Organometallics	D/U	D/U
Phenols	Durability: decrease (destructive action occurs over a long time period)	D/U
Organic esters	D/U	D/U

Source: Spooner et al. 1984.
Note: D/U = data unavailable.

TABLE 24. DOCUMENTED INTERACTIONS BETWEEN ORGANIC S/S BINDERS AND SPECIFIC CHEMICAL GROUPS

Chemical group	Polymers				
	Phenolic	Urethane	Urea-formaldehyde	Epoxy	Polyester
Organic compounds					
Alcohols & glycols	D/U	Set time: decrease Durability: no significant effect	D/U	Durability: no significant effect	Durability: no significant effect
Aldehydes & ketones	Set time: decrease Durability: no significant effect	Durability: decrease (destructive action occurs over a long time period)	D/U	D/U	D/U
Aliphatic & aromatic hydrocarbons	Durability: decrease (destructive action occurs over a long time period) Low molecular weight polymers only	Durability: no significant effect	Set time: increase Durability: no significant effect	Durability: decrease (destructive action occurs over a long time period)	Durability: decrease (destructive action occurs over a long time period)
Amides & amines	D/U	Durability: decrease (destructive action begins within a short time period)	D/U	D/U	D/U
Chlorinated hydrocarbons	Durability: decrease (destructive action occurs over a long time period)	Durability: no significant effect	Set time: increase (lengthen or prevent from setting) Durability: no significant effect	Durability: decrease (destructive action occurs over a long time period)	Durability: decrease (destructive action occurs over a long time period)

(Continued)

Source: Spooner et al. 1984.
Note: D/U = data unavailable.

TABLE 24. (Concluded)

Chemical group	Polymers				
	Phenolic	Urethane	Urea-formaldehyde	Epoxy	Polyester
Organic compounds					
Ethers & epoxides	D/U	Durability: no significant effect	Durability: decrease (destructive action occurs over a long time period)	D/U	D/U
Heterocyclics	D/U	D/U	D/U	D/U	D/U
Nitriles	D/U	D/U	D/U	D/U	D/U
Organic acids & acid chlorides	D/U	Set time: increase (lengthen or prevent from setting) Durability: no significant effect	Set time: no significant effect Durability: no significant effect	Durability: decrease (destructive action occurs over a long time period)	Durability: decrease (destructive action occurs over a long time period)
Organometallics	D/U	D/U	D/U	D/U	D/U
Phenols	Set time: increase (lengthen or prevent from setting) Durability: no significant effect	Durability: decrease (destructive action begins within a short time period)	D/U	D/U	D/U
Organic esters	D/U	D/U	D/U	D/U	D/U

TABLE 25. DOCUMENTED INTERACTIONS BETWEEN ORGANIC S/S BINDERS AND SPECIFIC INORGANIC CHEMICAL GROUPS

Chemical group	Bitumen	Silicate	Acrylamide	Polymer
				Phenolic
Heavy metals salts & complexes	Durability: decrease (destructive action occurs over a long time period)	Set time: decrease	Set time: increase (lengthen or prevent from setting)	D/U
Inorganic acids	Durability: no significant effect Nonoxidizing Except concentrated acids	Set time: decrease Durability: no significant effect	Set time: increase (lengthen or prevent from setting) Durability: decrease (destructive action begins within a short time period)	Durability: no significant effect Nonoxidizing
Inorganic bases	Durability: no significant effect	Set time: increase (lengthen or prevent from setting) Durability: decrease (destructive action begins within a short time period)	Set time: decrease Durability: decrease (destructive action occurs over a long time period)	Durability: decrease (destructive action occurs over a long time period)
Inorganic salts	Durability: decrease (destructive action occurs over a long time period)	Set time: decrease	Set time: decrease Durability: decrease (destructive action occurs over a long time period)	Set time: decrease Durability: no significant effect Except bleaches - Set time: decrease Durability: decrease (destructive action occurs over a long time period)

(Continued)

Source: Spooner et al. 1984.
Note: D/U = data unavailable.

TABLE 25. (Concluded)

Chemical group	Urethane	Urea-formaldehyde	Epoxy	Polyester
Heavy metals salts & Complexes	D/U	Durability: no significant effect	D/U	D/U
Inorganic acids	Set time: increase (lengthen or prevent from setting) Durability: decrease (destruction action begins within a short time period)	Set time: no significant effect Durability: decrease (destruction action occurs over a long time period)	Durability: no significant effect Nonoxidizing	Durability: no significant effect Nonoxidizing, except HF
Inorganic bases	Durability: decrease (destruction action occurs over a long time period)	Set time: increase (lengthen or prevent from setting) Durability: decrease (destruction action begins within a short time period)	Durability: no significant effect	Durability: decrease (destructive action occurs over a long time period)
Inorganic salts	Durability: decrease (destruction action occurs over a long time period)	Durability: no significant effect	Durability: no significant effect	Durability: no significant effect

TABLE 26. PREDICTED S/S BINDER COMPATIBILITIES WITH ORGANIC COMPOUNDS

Chemical group	Silicate	Acrylamide	Phenolic
Alcohols & glycols	Set time: no significant effect Durability: no significant effect	Set time: no significant effect	Set time: decrease Durability: increase
Aldehydes & ketones	Set time: no significant effect Durability: no significant effect	D/U	D/U
Aliphatic & aromatic hydrocarbons	Set time: no significant effect Durability: decrease (destructive action occurs over a long time period)	Set time: no significant effect	D/U
Amides & amines	Set time: decrease Durability: no significant effect	Set time: decrease Durability: decrease (destructive action occurs over a long time period)	Set Time: decrease Durability: increase
Chlorinated hydrocarbons	Set time: no significant effect Durability: decrease (destructive action occurs over a long time period)	Set time: no significant effect	D/U
Ethers & epoxides	Set time: no significant effect Durability: no significant effect	Set time: no significant effect	Set time: no significant effect Durability: no significant effect
Heterocyclics	Set time: no significant effect Durability: decrease (destructive action occurs over a long time period)	Set time: no significant effect	Set time: no significant effect Durability: no significant effect
Nitriles	Set time: no significant effect Durability: no significant effect	Set time: decrease	Set time: no significant effect Durability: no significant effect
Organic acids & acid chlorides	Set time: no significant effect	D/U	Set time: decrease
Organometallics	Set time: no significant effect Durability: no significant effect	Set time: decrease Durability: no significant effect	D/U
Phenols	Set time: no significant effect Durability: no significant effect	Set time: no significant effect Durability: no significant effect	D/U
Organic esters	D/U	D/U	D/U

Source: Spooner et al. 1984.
Note: D/U = data unavailable.

TABLE 27. PREDICTED POLYMER S/S BINDER COMPATIBILITIES WITH ORGANIC COMPOUNDS

Chemical group	Urethane	Urea-formaldehyde	Epoxy	Polyester
Alcohols & glycols	D/U	Set time: no significant effect	Set time: no significant effect	Set time: no significant effect
Aldehydes & ketones	Set time: no significant effect	D/U	Set time: no significant effect Durability: no significant effect	Set time: no significant effect Durability: no significant effect
Aliphatic & aromatic hydrocarbons	Set time: no significant effect	D/U	Set time: no significant effect	Set time: no significant effect
Amides & amines	Durability: no significant effect	Set time: no significant effect Durability: no significant effect	Set time: no significant effect Durability: no significant effect	Set time: decrease Durability: no significant effect
Chlorinated hydrocarbons	Set time: no significant effect	D/U	Set time: no significant effect	Set time: no significant effect
Ethers & epoxides	Set time: no significant effect	D/U	Set time: no significant effect Durability: no significant effect	Set time: no significant effect Durability: no significant effect
Heterocyclics	Set time: no significant effect Durability: no significant effect	Set time: no significant effect Durability: no significant effect	Set time: no significant effect Durability: no significant effect	Set time: no significant effect Durability: no significant effect
Nitriles	Set time: no significant effect Durability: no significant effect	Set time: no significant effect Durability: no significant effect	Set time: no significant effect Durability: no significant effect	Set time: no significant effect Durability: no significant effect
Organic acids & acid chlorides	Set time: increase (lengthen or prevent from setting)	D/U	D/U	Set time: no significant effect

(Continued)

Source: Spooner et al. 1984.
Note: D/U = data unavailable.

TABLE 27. (Concluded)

Chemical group	Urethane	Urea-formaldehyde	Epoxy	Polyester
Organometallics	D/U	Set time: no significant effect Durability: no significant effect	Set time: no significant effect Durability: no significant effect	Set time: decrease If metal is capable of acting as an accelerator
Phenols	Set time: increase (lengthen or prevent from setting)	Set time: no significant effect Durability: no significant effect	Set time: no significant effect Durability: no significant effect	Set time: no significant effect
Organic esters	D/U	D/U	D/U	Set time: no significant effect Durability: decrease (destructive action occurs over a long time period)

TABLE 28. PREDICTED S/S BINDER COMPATIBILITIES WITH INORGANIC COMPOUNDS

Chemical group	Silicate	Acrylamide	Phenolic
Heavy metal salts & complexes	Durability: no significant effect	D/U	D/U
Inorganic acids	D/U	D/U	Set time: increase (lengthen or prevent from setting)
Inorganic bases	D/U	D/U	Set time: decrease
Inorganic salts	Durability: decrease (destructive action occurs over a long time period)	D/U	D/U

Source: Spooner et al. 1984.
Note: D/U = data unavailable.

TABLE 29. PREDICTED POLYMERIC GROUT COMPATIBILITIES WITH INORGANIC COMPOUNDS

Chemical group	Urethane	Silicate	Acrylamide	Phenolic
Heavy metal salts & complexes	Set time: decrease If metal is capable of acting as an accelerator	D/U	Set time: decrease	Set time: decrease
Inorganic acids	D/U	D/U	Set time: no significant effect	Set time: no significant effect
Inorganic bases	D/U	D/U	D/U	Set time: decrease
Inorganic salts	D/U	D/U	D/U	D/U

Source: Spooner et al. 1984.
Note: D/U = data unavailable.

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APPENDIX A

ANNOTATED BIBLIOGRAPHY - EFFECTS OF ADDITIVES IN PORTLAND CEMENT

ABNORMAL SET OF PORTLAND CEMENT CAUSES AND CORRECTIVES

Kalousek, G. L.
Bureau of Reclamation, Denver, CO, Office of the Chief Engineer
Corp. Source Codes: 401851
Report No.: REC-OCE-69-2; GENERAL-45
Nov 69 29 p
NTIS Prices: PC A03 MF A01 Journal Announcement: USGRDR7004

Abnormal set of portland cement may be due to different combinations of several causes. Gypsum recrystallization was confirmed as one cause. The rate of ettringite precipitation of certain cements treated with organic admixtures correlated with the rate of stiffening of the mortars. Thixotropic set was determinable on cement-benzene slurries with a thixometer, an instrument developed for the purpose. Thixotropic behavior was induced by aeration at 50 percent relative humidity and persisted in cement-water pastes from about 10 seconds to over 11 minutes. The rate of gypsum and ettringite formation was followed by differential thermal analysis. The causes of and correctives for abnormal set are described.

Descriptors: Cements, hardening, crystallization; cements, differential thermal analysis, gypsum, test methods, recrystallization; sulfonates; calcium compounds; aluminates; hydrates.

Identifiers: Portland cements, cement additives, thixotropy, lignosulfonates, calcium aluminates, clinker.

Section headings: 11B (Materials--Ceramics, Refractories and Glasses); 13C (Mechanical, industrial, civil, and marine engineering--Construction Equipment Materials and Supplies).

ADSORPTION OF CALCIUM LIGNOSULFONATE ON TRICALCIUM ALUMINATE AND ITS HYDRATES IN A NONAQUEOUS MEDIUM

Ramachandran V. S.; Feldman, R. F.
National Res Council of Canada, Ottawa, Ont.
Cem Technol v 2 n 4 July-Aug 1971 p 121-9

It has been recognized that small amounts of some organic chemicals used as admixtures to Portland cement influence the properties of cement in terms of water requirements, setting time, strength, shrinkage, sulfate resistance, etc. Tricalcium aluminate, hexagonal calcium aluminate, and cubic aluminate hydrate were treated with calcium lignosulfonate, using dimethyl sulfoxide as the solvent. Adsorption was almost nil on the C//3A and the cubic phase. The hexagonal phase adsorbs irreversibly about 2.2% calcium lignosulfonate. (31 refs.)

Descriptors: Cement admixtures

Identifiers: Organic admixtures

Classification Codes: 412

EARLY HYDRATION OF CEMENT CONSTITUENTS WITH ORGANIC ADMIXTURES

Lorprayoon, V.; Rossington, D. R.
Alfred Univ, NY
Cem Concr Res v 11 n 2 Mar 1981 p 267-277 CODEN: CCNRAI ISSN: 0008-8846

The hydration of C_2S, C_3S, C_3A, C_4AF, and Type I Portland cement in the presence of calcium lignosulfonate and salicylic acid was studied at a high (20/1) water-cement ratio.

Descriptors: Cement, hydration, concrete, admixtures.

Classification Codes: 412

EFFECT OF GLUCOSE AND CALCIUM GLUCONATE ON THE HYDRATION OF PORTLAND CEMENT.

Tenoutasse, N.; Singh, N. B.
Free Univ. of Brussels, Belg.
Indian J. Technol v 16 n 5 May 1978 p 184-189 CODEN: IJOTA8 ISSN: 0019-5669

The effects of glucose and calcium gluconate on the hydration of Portland cement have been studied using isothermal microcalorimetry, differential thermal analysis, and X-ray diffraction techniques. Chemical analysis of the liquid phase was also done during the course of hydration. The results obtained indicate that glucose and calcium gluconate influence the consumption of gypsum in different manners. Glucose accelerates the consumption of gypsum, whereas calcium gluconate inhibits the formation of calcium trisulphoaluminate. On the basis of the results, an attempt has been made to understand the mechanism of the action of organic admixtures on the hydration of cements. (19 refs.)

Descriptors: Cement hydration

Classification Codes: 412

O VILIYANII ORGANICHESKIKH KISLOT NA SKHVATYVANIE TAMPONAZHNYKH PORTLANDTSEMENTNYKA RASTVOROV PRI VYSOKIKH TEMPERATURAKH I KAVLENIYAKH (Effect of Organic Acids on Setting of Plug-Back Portland Cement Mortars at High Temperatures and Pressures)

Mamulov, F. G.; Loskutov, D. A.; Tikhomirov, A. A.
Krasnodar Corresp Inst of Soviet Trade, USSR
Izv Vyssh Uchebn Zaved Neft Gaz n 12 1977, p 9-12, CODEN: IVUNA2

The effect of organic acids of different classes on setting times of mortars at 100° C and 400 kgf/cm^2 is studied. It is shown that monobasic aliphatic hydroxy-acids with more than three oxo groups, monobasic aromatic phenoloacids, and dibasic and tribasic aliphatic hydroxy-acids show strong retarding properties at high temperatures and pressures. Monobasic aliphatic aminoacids belong to setting time accelerators. An explanation of the phenomenon of retardation of setting times by hydroxy-acids is given. (In Russian.)

Descriptors: Oil well cementing, cement setting, acids, organic compounds.

Identifiers: Organic acids.

Classification Codes: 511, 412, 804.

EFFECT OF SOLUTIONS OF HUMIC COMPOUNDS ON CONCRETE

Robertson, K. R.; Rashid, M. A.
Bedford Inst of Oceanogr, Dartmouth, Nova Scotia
Jour Am Conc Inst, v 73, n 10, Oct 1976, p 577-580 CODEN: JACIAX

The corrosive effect of humic acid on Portland cement concretes was investigated with a 10-ppm concentration of organic matter under conditions simulating fresh and salt water environments. Calcium, the most abundant cation in concrete, was released in the fresh and salt water systems containing humic additions at maximum concentrations of 28 and 96 ppm, respectively. The corresponding controls which were devoid of organic matter contained significantly lower calcium concentrations. The solubility of calcium increased rapidly within the first 4 days of experimental exposure and then leveled off. (11 refs.)

Descriptors: Concrete testing, concrete reinforcements, corrosion, calcium compounds.

Identifiers: Humic acids, organic compounds.

EVALUATION OF CONCRETE AS A MATRIX FOR SOLIDIFICATION OF SAVANNAH RIVER PLANT WASTE

Stone, J. A.
Du Pont de Nemours (E.I.) and Co., Aiken, SC, Savannah River Lab.
Corp. Source Codes: 2204000
Sponsor: Department of Energy
Report No.: CONF-780545-1 1978 21 p
Meeting of the American Ceramic Society, Detroit, MI, USA, 6 May 1978.
Document Type: Conference proceeding
NTIS Prices: PC A02/MF A01 Journal Announcement: GRAI7825 NSA0300
Contract No. EY-76-C-09-001

Some of the favorable and unfavorable characteristics of concrete as a matrix for solidification of Savannah River plant waste, as found in this study, are listed. Compressive strength and leachability of waste forms containing ^{90}Sr and alpha emitters are very good. The waste forms have reasonable long-term thermal stability up to 400° C, although water is evolved above 100° C. Long-term radiation stability of the solid, as measured by strength and leachability, is excellent. For the unfavorable characteristics, methods are available to overcome any problems these properties might cause. Leachability of ^{137}Cs can be reduced by additives such as zeolite. Steam generation can be reduced by an initial degassing step; however, radiolytic gassing may require further study. Set times can be retarded with additives. (10 figs.) (ERA Citation: 03:046907).

INCREASING THE DURABILITY OF CONCRETE BY ADDITIVES OF SILICON ORGANIC POLYMERS

Batrakov, V. G.
Bureau of Reclamation, Washington, DC.
Corp. Source Codes: 068950 1972 169 p
Trans. of Mono. Povyshenie Dolgovechnosti Betona Dobavkami Kremniiorganlcheskikh,
Polimerov, Moscow, 1968, 277 p. Sponsored in part by National Science Foundation,
Washington, DC, Special Foreign Currency Science Information Program.
Document Type: Translation
NTIS Prices: PC A08/MF A01 Journal Announcement: GRAI7309
Contract No.: NSF-C-466

The durability of concrete was studied with additives of silicon organic polymers under the complex action of cyclic freezing and thawing, wetting and drying, capillary suction and evaporation of salt solutions, and also the prolonged continuous action of an aggressive liquid medium. The physicomechanical properties of concrete with silicon polymer additives were studied. The physicochemical aspects of the interaction of silicon-organic polymers of the polyhydrosiloxane and sodium siliconate type with the minerals of Portland cement, clinker, and cements were investigated.

INTERACTION BETWEEN CEMENT AND ORGANIC POLYELECTROLYTES

Kond, Renichi; Daimon, Masaki; Sakai, Etsuro
Tokyo Inst of Technol, Meguroku, Jpn
Cemento v 75 n 3 Jul-Sep 1978, p 225-230 CODEN: CEMEAM ISSN: 0008-8900

The influences of polyelectrolytes on the rate of hydration of Portland cement and alite and also on the dispersion of Portland cement were investigated by means of conduction calorimetry, sedimentation velocity, and adsorbed amount of polyelectrolytes. In the hydration of Portland cement and alite, the retarding effect gradually increased with increasing amount of polyelectrolytes. The retardation of cement hydration was ascribed to the adsorption of polyelectrolytes on the cement particle. (21 refs.)

Descriptors: Cement, hydration, polyelectrolytes.

Identifiers: Portland cement.

Classification Codes: 412, 815

INTERACTIONS OF ORGANIC COMPOUNDS IN PORTLAND CEMENT PASTES

Hansen, W. C.
Journal of Materials, Dec 1970, Vol 5, No. 4, pp 842-855, 3 tab, 22 refs
SUBFILE: HRIS

A review of the literature leads to the conclusion that tricalcium aluminate can combine with calcium salts of both low and high molecular weight organic acids to yield compounds similar to compounds formed with calcium salts of inorganic acids. It is suggested that the so-called adsorption of such organic salts by tricalcium aluminate is actually a chemical reaction with the formation of these complex salts. On the other hand, it appears that bi- and tricalcium silicates do not undergo similar reactions with these organic salts, but do adsorb them by either ionic or hydrogen bonding in a reversible manner. This makes it possible for tricalcium aluminate to remove these materials from the surfaces of the calcium silicates and thus terminate the retarding actions of these admixtures in cement pastes.

COMPOSIZIONE DELLA MASSA INTERSTIZIALE E IRREGOLARITA DI PRESA DI CEMENTI PORTLAND (Interstitial Mass Composition and Setting Irregularities of Portland Cements)

Costa, Umberto; Massazza, Franco
Cemento v 72 n 4 Oct-Dec 1975, p 181-194 CODEN: CEMEAM

A series of cements made in the same plant has shown unsteady setting irregularities when clinker contained higher quantities of CO_2. It has also been found that the CO_2 content is about inversely proportional to that of SO_3. The set time reduction in the irregular samples is accompanied by a delayed ettringite formation. Tests carried out have proved that the cause of the phenomena is due to the presence of alkali carbonates in relatively high concentrations. The influence of the clinker carbonates in the hydration process is equivalent to that of the same compounds added to cement. The setting irregularities can be eliminated by adding calcium hydroxide or calcium sulphate hemihydrate to cements. (16 refs.) (In Italian and English.)
Descriptors: Cement, setting, alkaline earth compounds.
Identifiers: Portland cement, ettringite, clinker.
Classification Codes: 412, 804.

MATERIALS

Cook, Wayne D.; Standish, Paul M.
Australian Dental Standards Lab, Abbotsford, Victoria, Aust.
J Biomed Mater Res v 17 n 2, Mar 1983 p 275-282 CODEN: JBMRBG ISSN: 0021-9304 Languages: English

The kinetics and mechanism of cure of resin-based restorative materials have been investigated by incorporating into commercial materials additional amounts of inhibitor initiator and accelerator. The polymerization was monitored by IR spectroscopy, viscosity measurements, and an oscillating rheometer. The rate of initiation of the polymerization was found to be first order with respect to the initiator and accelerator concentration. The inhibitor was found to be responsible for the induction period during which no polymerization occurred. The duration of this period was proportional to the inhibitor concentration. It was also found that the efficiency of the inhibitor affected the difference between the initial and final set times so that with one particularly effective inhibitor a "snap set" behavior could be obtained. (18 refs.)

MEASUREMENT AND CONTROL OF CEMENT SET TIMES IN WASTE SOLIDIFICATION

Stone, J. A., d'Entremont, P. D.
Du Pont de Nemours (E.I.) and Co., Aiken, SC, Savannah River Lab.
Corp. Source Codes: 2204000
Sponsor: Energy Research and Development Administration. Sep 76 16 p
NTIS Prices: PC A02/MF A01 Journal Announcement: GRAI7710 NSA0200
Contract No.: E(07-2)-1

Fixation of radioactive waste in concrete was investigated on laboratory scale. Some cement formulations containing simulated or actual sludges from the Savannah River Plant had set times that would be too short for reliable handling in plant equipment. Set times could be controlled by use of excess water, but the concrete forms produced had inferior strength. A commercial organic retarder was found to be effective for increasing set times of cement-sludge formulations. However, the dosage of retarder required to control set times of high-alumina cement formulations was 1.0 to 1.5 wt percent of dry solids, which is 5 to 10 times the normal dosage for Portland cements. Data were obtained to predict the optimum content of retarder and water. (ERA Citation 02:012526).

MECHANICAL BEHAVIOR OF FRESH CONCRETE
Alexandridis, A.; Gardner, N. J.
Stone & Webster, Toronto, Ont.
Cem Concr Res v 11 n 3 May 1981 p 323-339 CODEN: CCNRAI ISSN: 0008-8846

The shear strength characteristics of fresh concrete were studied through the use of a triaxial compression apparatus on concrete cylinders 100 mm in diameter and 200 mm high at 21° and 4° C for set times ranging from 40 to 160 minutes. The set results were analyzed by the shear strength theories of Mohr-Coulomb and Rowe for each time-temperature combination. (5 refs.)

Descriptors: Concrete testing, hardness.

Classification codes: 412, 421.

MIX DESIGNS FOR FAST-FIX 1 CONCRETE

(Final technical rept. May-Sep 68)
Nosseir, S. B.; Katona, M. G.
Naval Civil Engineering Lab, Port Hueneme, CA.
Corp. Source Codes: 248150
Report No.: NCEL-TR-613
Feb 69 33 p
NTIS Prices: PC A03 MF A01 Journal Announcement: USGRDR6909
Contract No.: Y-F38.536.006.01.002

The purpose of this investigation was to obtain information required for the use of Fast-Fix 1 concrete as a structural material. In particular, the effects of concrete mix design parameters and aging were investigated to determine if varying them would permit attaining compressive strengths in excess of 2500 psi without the use of retarding agents. In addition, splitting tensile strength and compressive stress-strain relations were determined for standard control cylinders. Recommendations are presented in the form of design curves which enable one to design a mix for a specified compressive strength and set time.

906639 EL790106639

PROBLEMA PERERABOTKI I ZAKHORONENIYA ZHIDKIKH RADIOAKTIVNYKH OTKHODOV ATOMNYKH ELEKTROSTANTSII. (Problem of Processing and Disposal of Liquid Radioactive Wastes of Nuclear Power Plants)

Kulichenko, V. V.
All-Union Sci Res Inst of Inorg Master., USSR
Teploenergetika n 6 Jun 1978, p 20-23, CODEN: TRLOA5

At present, controlled collection and storage of liquid wastes is implemented at all the nuclear plants in the USSR. Ion-exchange resins and material of wash-on filters (pearlite, etc.) in the form of aqueous sludges are transferred for storage into special stained steel containers placed in reinforced concrete canyons. Problems of deepwell disposal are discussed. Solidification by means of cementation is rejected as too costly, and bituminization tests in the USSR are described. A possibility of substituting asphalt for bitumen is pointed out. (11 refs.) (In Russian.)

PRODUCTS FORMED IN AGED Ca-POLYESTER COMPLEXED POLYMER CONCRETE CONTAINING CEMENT PASTE

Sugama, T.; Kukacka, L. E.
Brookhaven National Lab., Upton, NY
Corp. Source Codes: 004545000; 0936000
Sponsor: Dept. of Energy, Washington, DC Report No.: BNL-31172 Mar 82
21 p
Languages: English NTIS Prices: PC A02/MF A01 Jour Announ: GRAI8314
NSA0800
Country of Publication: United States
Contract No.: AC02-76CH00016

Poorly crystallized calcium hydroxide (CA$(OH)_2$) yielded from Portland cement pastes incorporated in calcium-polyester complexed polymer concrete was slowly formed during 21 days exposure in water at 24° C. Crystal growth continued as the hydration reactions proceeded. Ca$(OH)_2$ formed within the amorphous organic polymer layers after up to 90 days exposure had little if any effect on the ultimate strength of the PC composites. Ca^{2+} ions increased with exposure time, and they act as strongly nucleophilic agents to enhance the formation of complexed COO^- (Ca^{2+}) groups. These contain an ionic bond between Ca^{2+} ion and carboxylate anion (COO^-) produced by the hydrolysis of esters in UP polymer. (10 figs.) (ERA Citation 08:010303).

PROPERTIES OF RADIOACTIVE WASTES AND WASTE CONTAINERS

(Quarterly progress rept. Jul-Sep 80)
Morcos, Nabil; Weiss, Allen J.; Adams, J. W.; Chan, S. F.; Hayde, P. R.
Brookhaven National Lab., Upton, NY Corp. Source Codes: 004545000
Sponsor: Nuclear Regulatory Commission, Washington, DC
Office of Nuclear Regulatory Research. Rep No.: BNL-NUREG-51316 Jun 81
74 p
See also NUREG/CR-1694 Languages: English
NTIS Prices: PC A04/MF A01 Journ. Announcement: GRAI8123
Country of Publication: United States Contract No.: DE-AC02-76CH00016

The following is reported on this quarter. (A) A study was initiated to evaluate the leachability and integrity of bitumen/organic ion exchange resin composites. Mixtures of anionic and cationic resins in the SO4-S, H^+, Cs^+, and Sr^{+2} forms were used. (B) The leachability of cesium-137 from cement waste forms and cement/organic ion exchange resin (H^+ form) was studied. Portland II and lumnite cements were used in making the forms. (C) An experiment was initiated to study aqueous media as a function of ionic species and their concentrations in an aqueous milieu. The species studied were cesium, strontium, and aluminum. (D) As a consequence of the water decontamination from the auxiliary building at TMI-II, ion exchange media containing abnormally high loadings of ^{137}Cs are presently stored in the dewatered state pending a decision for their safe disposal. Organic ion exchange resins are known to undergo radiation damage. The areas investigated with respect to radiation damage to ion exchange materials were: pH change, agglomeration, generation of gases, and corrosion of mild steel used to contain the ion exchange media. Results of a scoping study performed at Pennsylvania State University, under subcontract to Brookhaven National Laboratory are presented.

REACTION MECHANISM OF ORGANIC ADMIXTURES WITH HYDRATING CEMENT COMPOUNDS

Young, J. F. Illinois University, Urbana
Transportation Research Record N564 pp 1-9 12 fig, 1 tab, 29 ref 1976
Available from: Transportation Research Board Publications Office,
2101 Constitution Ave., NW, Washington, DC 20418

This paper discusses the possible mechanisms by which organic compounds influence the setting properties of Portland cement. From a consideration of the hydration mechanisms of tricalcium silicate and tricalcium aluminate, it is concluded that organic compounds influence the hydration of these compounds by their effect on the hydration products through complexing and nucleation processes. It is hypothesized that the hydration of tricalcium silicate is controlled by the nucleation and growth of calcium hydroxide. The poisoning of nuclei by soluble silica is responsible for the induction period. Adsorption of organic compounds onto calcium hydroxide nuclei, through a chelating process, inhibits crystal growth even more effectively and prolongs the induction period. Tricalcium aluminate is considered to hydrate rapidly because the protective hydrate layer is destroyed by conversion to the hydrate of tricalcium aluminate. Organic retarders enter the interlayer region of the hexagonal hydrates to inhibit this conversion reaction and therefore maintain the integrity of the hydration barrier. A similar mechanism may hold in the presence of sulfate ions. In Portland cement, adsorption of admixtures by the hydration products of tricalcium aluminate controls the supply of admixture to tricalcium silicate. This explains the enhanced retardation when the addition of admixtures is delayed after the first addition of water.

RESISTANCE OF PORTLAND CEMENT MORTAR TO CHEMICAL ATTACK - A PROGRESS REPORT

Kuenning, W. H.
Highway Research Record, Hwy Res Board 1966 No. 113, pp 43-87, 7 fig, 14 tab, 37 ref.

An extensive study to furnish information about the resistance of concrete to chemical attack by various inorganic and organic compounds has been undertaken using 1.5 - by 1.5- by 10-cm mortar bars. Changes in length, weight, and sonic modulus are measured periodically. The study is designed to determine relative resistance to chemical attack of various special type mortars/microconcretes at water-cement ratios representative of full-scale concretes. It also furnishes information which may help explain the mechanisms of attack by specific agents. About 1,200 specimens have been placed under test; many have been exposed for more than 2 years. Most are still in satisfactory condition. Those failures which have occurred represent one of two main kinds of attack, or sometimes both. The first is removal of soluble compounds from cement by acid, sequestering agent, or exchangeable ion. The second is the deposition of new compounds within the paste. Rates of attack are compared and the nature of the attack by various groups of substances is discussed.

REVIEW OF THE MECHANICS OF SET-RETARDATION IN PORTLAND CEMENT PASTES CONTAINING ORGANIC ADMIXTURES

Young, J. F.
Cement and Concrete Research, Vol 2, No. 4, Jul 1972, pp 45-33.

Various mechanisms have been proposed to explain how organic admixtures affect the hydration of cement clinker compounds. These are reviewed and discussed critically. Complex formation between the organic compounds and aluminate or silicate ions may enhance the initial reactivity of the anhydrous compounds. Set-retardation may be primarily due to retarding of the hydration of tricalcium silicate through the adsorption of organic admixtures onto calcium hydroxide nuclei. Adsorption onto the initial hydration products of tricalcium aluminate can also retard further hydration.

REVIEW OF RADIOACTIVE WASTE IMMOBILIZATION IN CONCRETE

Lokken, R. O.
Battelle Pacific Northwest Labs., Richland, WA Corp. Source Codes: 9500022
Sponsor: Department of Energy. Jun 78 112 p. Languages: English
NTIS Prices: PC A06/MF A01 Journal Announcement: GRAI7905 NSA0400
Contract No.: EY-76-C-06-1830

A discussion is given of properties of concrete waste forms as obtained through research on immobilization of radioactive wastes in concrete. Types of radioactive waste discussed include low-level and intermediate-level radioactive waste, simulated defense high-level waste (HLW) sludges and calcines, simulated neutralized AGNS acid fuel reprocessing waste, and simulated power reactor fuel cycle HLW calcines. The waste form properties include water-cement ratio, set times, curing exotherms, compressive strength, impact strength, Sr/Cs/transuranics leachabilities, thermal conductivity, thermal stability, and radiation stability. A discussion is also given of the conditions and restrictions that govern the feasibility of immobilizing HLW in concrete. Results of theoretical calculations are discussed and illustrated, as are the effects of waste loading on material requirements. Properties of glass and concrete waste forms and of hot-pressed cement used for the solidification are compared. A conceptual process for HLW immobilization in concrete is discussed with emphasis on processing problems associated with heat and radiation effects on water. Use of hydraulic cements for the solidification of low heat generating wastes will produce a product with acceptable properties; the high heat generating rates and radioactivity of HLW make feasibility assessment difficult. Hot-pressed cement may make HLW immobilization feasible. (27 tables, 21 figures, 70 references.)
(ERA Citation 04:000367).

SOLIDIFICATION OF OILS AND ORGANIC LIQUIDS

Clark, D. E.: Colombo, P.; Neilson, R. M., Jr.
Brookhaven National Lab., Upton, NY Corp. Source Codes: 004545000; 0936000
Sponsor: Department of Energy, Washington, CE Report No.: BNL-51612
Jul 82 31 p Languages: English
NTIS Prices: PC A03/MF A01 Journal Announcement: GRAI8317 NSA0800
Country of Publication: United States Contract No. AC02-76CH0016

The suitability of selected solidification media for application in the disposal of low-level oil and other organic liquid wastes has been investigated. In the past, these low-level wastes (LLW) have commonly been immobilized by sorption onto solid absorbents such as vermiculite or diatomaceous earth. Evolving regulations regarding the disposal of these materials

encourage solidification. Solidification media that were studied include Portland type I cement; vermiculite plus Portland type I cement; Nuclear Technology Corporation's Nutek 380-cement process; emulsifier, Portland type I cement-sodium silicate; Delaware Custom Materiel's cement process; and the US Gypsum Company's Envirostone process. Waste forms have been evaluated as to their ability to reliably produce free-standing monolithic solids that are homogeneous (macroscopically), contain <1 percent free-standing liquids by volume, and pass a water immersion test. Solidified waste form specimens were also subjected to vibratory shock testing and flame testing. Simulated oil wastes can be solidified to acceptable solid specimens that have volumetric waste loadings of less than 40 volume-%. However, simulated organic liquid wastes could not be solidified into acceptable waste forms above a volumetric loading factor of about 10 volume-% using the solidification agents studied.
(ER Citation 08-023118)

SOLIDIFICATION OF SIMULATED TRANSURANIC CONTAMINATED INCINERATOR ASH WASTES USING PORTLAND TYPE I CEMENT

Neilson, Jr., R. M.; Colombo, P.
Brookhaven National Lab., Upton, NY Corp. Source Codes: 0936000; 9500022
Sponsor: Battelle Pacific Northwest Labs., Richland, WA, Dept. of Energy.
May 78 24 p Languages: English NTIS Prices: PC A02/MF A01
Journal Announcement: GRAI7905 NSA0300 Contract No.: EY-76-C-02-0016

A preliminary study was performed to investigate the use of hydraulic cement for the solidification of transuranic (TRU) contaminated incinerator ash wastes. In this work, the compositional phase fields in which acceptable solidification is obtained using Portland type I cement were determined for three simulated TRU incinerator ash wastes. These wastes include Battelle Northwest TRU incinerator ash, Rocky Flats plutonium recycle TRU incinerator ash, and Mound Laboratory cyclone incinerator TRU ash ($11A^2$). The compressive strengths and set times of selected formulations were measured.
(ERA Citation 03:054701)

STRUCTURE AND PROPERTIES OF PORTLAND CEMENT CLINKER DOPED WITH ZINC OXIDE

Odler, Ivan; Schmidt, Otto
Tech Univ Clausthal, Ger
J Am Ceram Soc v 63 n 1-2 Jan-Feb 1980 p 13-16 CODEN: JACTAW
ISSN: 0002-7820

The effect of ZnO on the structure of Portland cement and its properties has been investigated. Zinc oxide accelerates the rate of Portland clinker formation. The results show that the initial rate of tricalcium silicate hydration is retarded and the formation of ettringite is moderately accelerated in cements made from ZnO-doped clinkers. The set time of these cements is gradually prolonged and their strength development is retarded with increasing degrees of ZnO doping. (4 refs.)

Descriptors: CEMENT, Additives Classification Codes: 412

VOLUME REDUCTION OFFERS RADWASTE-DISPOSAL BENEFITS

Eggett, Donald R.; Enegess, David N. Commonw Edison Co., USA
Power v 126, n 10, Oct 1982, p 57-59, CODEN: POWEAD ISSN: 0032-5929

Disposing of radioactive waste generated at nuclear stations continues to pose a challenging national problem. A significant portion of this waste is made up of ion-exchange resins used in plant water and wastewater-treatment operations. Rising shipping costs are adding to the problem of dwindling burial sites, providing strong economic incentives for reduction of radwaste volumes. Under options available, spent resins are dewatered or solidified with cement before shipment. Cement solidification has the effect of actually increasing the already-high waste volume to be removed for burial. A test program is presented that evaluates the feasibility of a volume reduction and solidification process that mixes dried wastes with a binder, normally asphalt. (3 refs.)

WASTE-FORM DEVELOPMENT PROGRAM. ANNUAL PROGRESS REPORT, OCTOBER 1980 - SEPTEMBER 1982

Neilson, Jr., R. M.; Colombo, P.
Brookhaven National Lab., Upton, NY
Corp. Source Codes: 004545000; 0936000
Sponsor: Dept of Energy, Washington, CE
Report No.: BNL-51614
Sep 82 147 p Languages: English
NTIS Prices: PC A07/MF A01 Journal Announcement: GRAI8317 NSA0800
Country of Publication: United States
Contract No.: AC02-76CH00016

Low-level wastes (LLW) at nuclear facilities have traditionally been solidified using Portland cement (with and without additives). Urea-formaldehyde has been used for LLW solidification, while bitumen (asphalt) and thermosetting polymers will be applied to domestic wastes in the near future. Operational difficulties have been observed with each of these solidification agents. Such difficulties include incompatibility with waste constituents inhibiting solidification, premature setting, free-standing water, and fires. Some specific waste types have proven difficult to solidify with one or more of the contemporary agents. Similar problems are also anticipated for the solidification of new wastes, which are generated using advanced volume-reduction technologies, and with the application of additional agents which may be introduced in the near future for the solidification of LLW. In the Waste Form Development Program, contemporary solidification agents are being investigated relative to their potential applications to major fuel cycle and nonfuel cycle LLW streams. The range of conditions under which these solidification agents can be satisfactorily applied to specific LLW streams is being determined. These studies are primarily directed toward defining operating parameters for both the improved solidification of problem wastes such as ion exchange resins, organic liquids and oils for which prevailing processes, as currently employed, appear to be inadequate, and the solidification of new LLM streams, including high solids-content evaporator concentrates, dry solids, and incinerator ash generated from advanced volume-reduction technologies. Solidified waste forms are tested and evaluated to demonstrate compliance with waste form performance and shallow land burial (SLB) acceptance criteria and transportation requirements (both as they currently exist and as they are anticipated to be modified with time). (ERA Citation 08:019818)

Descriptors: Radioactive waste processing, solidification, low-level radioactive wastes, Portland cement, bitumens, research programs, ashes, ion exchange materials, nitrates, polymers, additives, resins, compressibility.

Identifiers: ERDA/052001; NTISDE

Section Headings: 18G (Nuclear Science and Technology--Radioactive Wastes and Fission Products); 77G (Nuclear Science and Technology--Radioactive Wastes and Radioactivity).

APPENDIX B

ANNOTATED BIBLIOGRAPHY - EFFECTS OF ADDITIVES ON ASPHALT

Michaels, A. S.; Puzinauskas, V.

Highway Research Board Bulletin 1956 No. 129, pp 26-49, 14 Fig, 13 Tab.
SUBFILE: HRIS

The effect of certain selected chemical additives in low concentration (less than 1 percent by weight) on the stabilization of fine-grained soil (a clayey silt from Massachusetts) with asphalt was examined. Soil samples were stabilized with either asphalt-gasoline cutbacks or asphalt-in-water emulsions, the chemical additives examined either being incorporated with the asphalt, or used to pretreat the soil before asphalt addition. Properties of the stabilized soil examined were primarily unconfined compressive strength after curing, and compressive strength and water absorption after water immersion. It was found that the addition of phosphorous pentoxide, certain epoxy resins, and certain organic isocyanates to asphalt cutback significantly improved the strength characteristics of asphalt stabilized soil. Addition of antistripping additives to asphalt cutback was found generally to reduce strength and increase water absorption; however, pretreatment of soil with such additives before incorporation of asphalt cutback was found to have a beneficial effect on strength and water resistance. Soil stabilized with asphalt emulsions containing soap as the emulsifier was found to have quite high dry strength, but the strength after water immersion was far lower than that of cutback-stabilized soil. On the other hand, soil stabilized with emulsions containing antistripping additives as emulsifiers exhibited wet strengths comparable to, and, in some instances, superior to those stabilized with cutback. Mixing-water content and type of emulsifier appear to be major factors affecting stabilization. It is concluded from this work that chemical additives hold considerable promise in asphalt stabilization practice, offering opportunities for broader and more effective use of asphalt for treatment of fine-grained soils.

0247146 EIM8401008146
ASPHALT FIXATION OF HAZARDOUS WASTES CONTAINING HEAVY METAL SALTS
Kulkarni, Ramchandra K.; Rosencrance, Alan B.

US Army Medical Bioengineering Research & Development Lab, Fort Detrick, Fredrick, MD, USA
186th National Meeting - American Chemical Society, Division of Environmental Chemistry, Vol 23, No. 2, Washington, DC, USA, Aug 28-Sep 2 1983.
Sponsor: ACS, Div of Environmental Chemical, Washington, DC, USA
Source: National Meeting - American Chemical Society, Division of Environmental Chemistry 186th, v 23 n 2 1983. Publ by ACS, Washington, DC, USA, p 127-130

ISSN: 0270-3009 CODEN: NMACDY

Languages: English Conf. No.: 03436

Descriptors: Industrial Wastes-Treatment

Identifiers: Abstract only; paint removal; metal finishing: electroplating; effluent water precipitation; heavy metal hydroxides/sulfides; stable matrice fixation; solidification disposal; microencapsulation; organic polymers/asphalt: sanitary landfill site disposal.

Classification Codes: 452; 453; 802

232918 DA
ASPHALTIC BINDER STABILIZED ROADS

Reagel, F. V.

Highway Research Board Proceedings 1983 Vol 18, Part II, pp 292-298.
SUBFILE: HRIS

Soil stabilization is "the treatment of soils with admixtures which either introduce or increase a certain stability element (gravel and sand for friction and interlocking action) or change the soil as a result of physico-chemical reaction." The purpose of these admixtures is to provide a soil system that is stable under all climatic conditions and traffic. One of the simplest methods of chemical stabilization involves the surface application of road oil to earth surfaces at a rate of approximately 1 gallon per square yard, preferably in two or three increments. The suboiled method involves the use of a suboiling machine that consists of a four-wheeled tractor-drawn A-frame, 7-1/2 ft wide, on which are mounted 31 scarifier teeth. The purpose is to spread the granular material, if any is to be added, uniformly over the roadway so that it is ready for stabilization. The scarified layer is pulverized to the point that all material will pass freely between the suboiler teeth. The bituminous treatment agent is introduced at one or more depths along with a predetermined quantity of water, except for emulsions. For the road mix method, one of the differences is that the bituminous treating agent is applied in increments of 0.5 gal per square yard (for 5- to 6-in. base thickness). Each application is incorporated with the soil aggregate mixture, together with a sufficient amount of water by means of disks and gang plows.

ASPHALT PAVING TECHNOLOGY, VOLUME 47, 1978

Anon
Assoc of Asphalt Paving Technol, Univ of Minn., Minneapolis.
Asphalt Paving Technol. v 47. Proc. Assoc. Asphalt Paving Technol, Tech Sess, Lake Buena Vista, Fla., Feb 13-15 1978. Publ by Assoc. of Asphalt Paving Technol., Univ. of Minn., Minneapolis, 1978 770 p. CODEN: PRPTAA ISSN: 0066-9466

The proceedings contains 24 papers, all of which are indexed separately. Among the subjects covered are low-temperature rheology of asphalt cements, fatigue and rutting tests on bituminous base mixes, structural distress prediction in asphalt pavements, permanent deformation characteristics of cement-emulsion stabilized sand, effect of aggregate shape on bituminous mix character, adhesion between asphaltic concrete layers, creep test in asphalt mix design and in predicting pavement rutting, physico-chemical aspects of fillers in bituminous paving mixtures, and others. Also included are presentations made at a symposium on pavement rehabilitation maintenance and economics, which was held during the conference.

CHEMICAL DEMULSIFIATION OF NATURAL PETROLEUM EMULSIONS OF ASSAM (INDIA)

Sharma, I. C.; Hague, I.; Srivastava, S. N.
Dibrugarh Univ., India
Colloid Polym Sci v 260 n 6, Jun 1982, p 616-622, CODEN: CPMSB6 ISSN: 0303-402X

About one-third of the petroleum production of every oil field is in the form of water in oil emulsions which are naturally stabilized by the nickel and vanadium porphyrins from asphaltene portion of crude. The petroleum emulsions of Assam oil fields which have been taken for the present work are stabilized by the organometallic compounds of iron and high molecular weight compounds from asphaltenes. In the reported experiments, attempts were made to break the oil emulsions using polyoxyethylene alkyl phenols, their sulphonates and sodium sulphonates in different combinations. The nonyl and octyl phenols with 30 and 40 molecules of ethylene oxide were found to be the most effective demulsifiers. A simple method for calculating the chemical demulsification efficiency and a factor H/S paralleled to HLB and H/L for evaluating the emulsification property of surface active agents have been introduced. (35 refs.)

Descriptors: Emulsions, chemical reactions, petroleum products: physical chemistry, colloid chemistry, polymers.

CLAY STABILIZATION IN SANDSTONES THROUGH ADSORPTION OF PETROLEUM HEAVY ENDS

Clementz, David M.
Chevron Oil Field Res Co., La Habra, Calif.
JPT J Pet Technol v 29 Sep 1977 p 1061-1066 CODEN: JPTJAM

This paper presents experimental evidence for a natural clay stabilization mechanism. It is based on the observation that petroleum heavy ends (primarily the asphaltenes and resins) adsorb tenaciously to clay surfaces and significantly alter the physical and chemical properties of the clay. Sandstone cores, which are normally extremely sensitive to fresh water, are stabilized effectively by treatment with hydrocarbon solutions of petroleum heavy ends. (10 refs.)

Descriptors: Oil well production, flooding, oil wells, sand consolidation, petroleum reservoir engineerings, core analysis, clay.

Identifiers: Formation damage, water flooding.

Classification Codes: 511; 512; 483.

THE EFFECT OF FLUX-OIL AND TRINIDAD LAKE ASPHALT CONTENT ON THE PHOTO-OXIDATION OF ASPHATLIC CEMENTS

Shields, C. F.
Road Research Lab., Crowthorne (England).
Report No.: RRL-LR120 1967 13 p
NTIS Prices: PC A02 MF A01 Journal Announcement: USGRDR6810

The Note gives the results of an investigation into the effect of flux-oil and/or Trinidad Lake Asphalt content on the photo-oxidation of asphaltic cements. The investigation showed that (a) a bitumen, "cut-back" to a particular viscosity with flux-oil, developed the same surface texture and produced the same amount of water-soluble material as a straight-run bitumen of the same viscosity and (b) the surface texture developed by blends of Trinidad Lake Asphalt and petroleum bitumen is influenced by the percentage of Trinidad Lake Asphalt in the blend and the sources of the crude oil from which the bitumen was produced.

EVALUATION OF THE USE OF ANTISTRIPPING ADDITIVES IN ASPHALTIC CONCRETE MIXTURES

(Research Rept).
Arena, Philip J., Jr.; Ashby, J. T., Jr.,
Louisiana Dept. of Highways, Research and Development Section.
Report No.: RR-46. Jan 70, 26 p.
NTIS Prices: PC A03 MF A01 Journal Announcement: USGRDR7021
Contract No.: LDH-68-3B(B); HPR-1(7)

The study was initiated to ascertain if antistripping additives would have any beneficial effect in combating stripping. After preliminary tests, one additive was selected for further evaluation and testing. Comparative tests were conducted on the asphaltic cement and hot mix with and without the additive. These tests included: Marshall immersion, gyratory shear stress and bearing resistance, roadway cores (specific gravity and percent compaction), and asphalt analysis. The results indicated that the additive had a negligible effect on the properties tested.

INCINERATOR RESIDUE IN ASPHALT BASE CONSTRUCTION

Haynes, Joseph A.; Ledbetter, William B.
Brown & Root, Inc., Houston, TX
ASCE Transp Eng J., v 103, n 5, Sep 1977, p 555-564 CODEN: TPEJAN

The construction and maintenance of the United States highway system has created an increasing demand for quality construction materials. In large urban areas, material scarcity, plus long transportation distances, has escalated the cost of suitable materials. In these areas there is an increasing supply of solid waste. This paper examines the use of incinerator residue obtained from the burning of municipal solid wastes as an aggregate in asphaltic concrete. Laboratory work followed by construction of a city street in Houston resulted in the following conclusions: (1) asphaltic concrete made with incinerator residue (termed littercrete) meets current specifications for asphalt stabilized base materials; (2) littercrete can be constructed using conventional equipment and technology; (3) the littercrete pavement has performed as well as the conventional blackbase control; and (4) littercrete offers an attractive economical advantage in certain areas. (14 refs.)

IMPROVEMENT OF ASPHALT-STABILIZED FINE-GRAINED SOILS WITH CHEMICAL ADDITIVES

Michaels, A. S.; Puzinauskas, V.
Highway Research Board Bulletin No. 204, pp 14-45, 11 Fig, 18 Tab, 2 Ref.
SUBFILE: HRIS

The effects of selected chemical additives upon the strength and water-resistance of asphalt-cutback-stabilized soils were determined. The effects of fatty amines and phosphorous pentoxide, in conjunction with asphalt, on soil stability were studied. The variables studied included soil type and/or plasticity additive and asphalt concentration, molding water content, curing and aging conditions, asphalt origin and hardness, cutback composition, and solvent. Treated soils were molded and statically compacted under controlled conditions, cured for specified periods in air with controlled relative humidity, and totally immersed in water for prescribed periods. The samples were tested in unconfined compression, and their densities and volatile contents measured by standard procedures. Successful stabilization was achieved by incorporation of small amounts of phosphorous pentoxide and of fatty amines with asphalt cutback into very fine-grained soils that could not be stabilized with asphalt alone. Coarser grained soils, which did develop some wet-stability with asphalt, were improved by addition of these additives. Molding water content was found to be an important variable affecting strength and water resistance. Asphalt cutbacks prepared with highly volatile solvents were found to be significantly better stabilizers than medium-curing cutbacks. A wide variety of acidic phosphorous-bearing compounds, when added in low concentrations to cutback-treated soils, were found to be even more effective stabilization aids than phosphorous pentoxide. Greatest improvements were observed with benzene phosphonic acid. A theory of the mechanism of asphalt-stabilization of soils and of additive-action was developed. It is concluded that the use of small amounts of appropriate chemical additives may make economically practicable the successful stabilization, with asphalt, of a broad spectrum of fine-grained, high-plasticity soils.

202857 DA
NEEDED RESEARCH ON ASPHALTIC ROAD MATERIALS

Kelley, E. F.; Crum, R. W.; Lang, F. C.; Cattell, R. A.; Campbell, L. C.; Boyd, J. E.; Baskin, C. M.
Highway Research Board Proceedings 1935 Vol 15, pp 261-272 SUBFILE: HRIS

The term "asphaltic materials," as used in this discussion, covers the range of liquid, semi-solid, and solid asphaltic products used in road construction. In chemical composition asphaltic materials are varied, and complex and almost numberless varieties may result from different materials and methods of refining. Some tests for asphaltic materials are intended to measure certain qualities directly; others are identification tests. Further research is necessary to determine in which category some tests belong. Investigation is also needed to determine if tests intended to measure quality actually do so. There is evidence to show that ductility tests and tests designed to control susceptibility to temperature changes are not directly related to service behavior. A high degree of durability is very important, and little concerning this quality can be foretold from present test methods. Further research is needed to determine how the characteristics of the crude oils influence the quality of the finished products. Closely allied with these questions are the problems which arise from different methods of refining. Heating, mixing, and placing asphaltic materials alter their characteristics. It is necessary to determine to what extent such changes may be permitted without damage to the quality of the finished product. It is also necessary to study the interrelation between asphaltic materials and the aggregates. Study is also needed on new uses for bituminous materials such as stabilization of soils. When the details of needed research are considered, the problem becomes enormously complex. The combined efforts of all interested in the production and use of these materials are required if results are to be achieved in a reasonable length of time.

SOLID RADWASTE EXPERIENCE IN EUROPE USING ASPHALT

Stewart, J. E.; Herter, Rainer
Werner & Pfleidere Corps., Waldwick, NJ ASME Pap n 75-Pwr-21 for Meet
Sep 28-Oct 1 1975, 12 p CODEN: ASMSA4

The process of solidifying radioactive wastes from nuclear power and reprocessing plants in Europe using the asphalt (bitumen) extruder-evaporator process is reviewed. A process description plus data on volume reduction, leachability, and flammability from research an actual operation at the three leading nuclear centers in Europe is presented. The world's first asphalt solidification system began operating in France in 1965. (6 refs.)

STABILIZED COPPER MILL TAILINGS FOR HIGHWAY CONSTRUCTION

Sultan, Hassan A.
Univ of Ariz., Tuscon
Transp. Res Board Transp Res Rec n 734 1979, p 1-7 CODEN: TRREDM

The results of an investigation to determine the feasibility of using stabilized copper mill tailings in road construction are presented. Properties of three types of tailing were evaluated after preliminary testing of several tailings from Arizona, Idaho, and Utah. The properties of the three tailings are summarized, and detailed results obtained for one type are reported. Index properties of the untreated tailings, including physical and mechanical properties, are given. Engineering parameters of untreated tailings are reported, including compaction characteristics; compressive, tensile, and shear strength; compressibility; permeability; and erodibility by rainfall. Properties of cement-stabilized and asphalt-stabilized tailings are also presented. (19 refs.)

URANIUM MILL TAILINGS STABILIZATION

Hartley, James N.; Koehmstedt, Paul L.; Esterl, David J.; Freeman, H. D.
Battelle, Pac Northwest Lab, Richland, WA.
Proc Symp Waste Manage '80, The State of Waste Disposal Technol,
Mill Tailings, and Risk Analys Models, v 1, Tucson, AZ, Mar 10-14, 1980.
Publ by Univ of Ariz, Coll of Eng., Tucson, 1980, p 193-20 CODEN: PSWMDY

One of the most promising concepts for stabilizing U tailings is the use of asphalt emulsion to contain radon and other hazardous materials within uranium tailings. Results of studies of Pacific Northwest Laboratory indicate that a radon flux reduction of greater than 99 percent can be obtained using either a poured-on/sprayed-on seal or an admixture seal containing about 18 wt percent residual asphalt. A field test was carried out in June 1979 at the Grand Junction tailings pile in order to demonstrate the sealing process. A reduction in radon flux ranging from 4.5 to greater than 99 percent (76 percent avg) was achieved using a 12.7-cm (5-in.) admix seal with a sprayed-on top coat. Following compaction, a spray coat seal was applied over the admix as the final step in construction of a radon seal.

USE OF AN EXTRUDER-EVAPORATOR TO STABILIZE AND SOLIDIFY HAZARDOUS WASTES

Doyle, Richard D.
Werner and Pfleiderer Corp., Waldwick, NJ
Proc Mid Atl Ind Waste Conf 11th, PA State Univ, University Park, Jul 15-17, 1979. Publ by PA State Univ, University Park, 1979, p 56-62 CODEN: MIWPD8
ISSN: 0544-0327

The paper discusses the volume reduction and solidification (VRS) system, utilizing an extruder-evaporator that was developed to meet the need for a process to handle a variety of chemical properties associated with the relatively low-volume, highly toxic wastes, such as arsenic, heavy metals, or electroplating type wastes. The system, designed to process liquid and solid wastes generated form industrial processes, produces a solidified end product with the hazardous constituents, regardless of their chemical characteristics, immobilized in a plastic binder. It handles a wide variety of liquid and dry waste feed streams, in conjunction with most plastic binders (asphalt, polyethylene, polypropylene, urea formaldehyde and vinyl polyesters). The extruded-evaporator, in one step, evaporates all unwanted solvent from the waste while homogenizing the waste constituents with the liquid plastic binder for discharge into a container. Once this waste-plastic mix has cooled, a significant volume reduction effect is realized. The paper describes the VRS system, binder characteristics and selection, and operating experiences.

USE OF HYDRATED LIME IN BITUMINOUS MIXTURES TO DECREASE HARDENING OF THE ASPHALT CEMENT
(Final rept)

Chachas, Catherine V.
Utah State Dept of Highways, Materials and Tests Div., Dec 71 81 p
NTIS Prices: PC A05/MF A01 Journal Announcement: GRAI7302

When asphaltic cement hardens, cracking and raveling occur which cause deterioration of the pavement. It was found that the addition of hydrated lime in bituminous mixtures decreases the rate of hardening of the asphalt, thereby prolonging the life of the pavement. The evaluation of the effects of hydrated lime on asphaltic pavements was based on viscosity measurements of the extracted asphalts because lowering of viscosity is an indication of reduction of hardness of the asphalt. Field and laboratory studies were conducted on combinations of asphalts and aggregates with and without hydrated lime. The viscosities of the asphalts extracted from bituminous mixtures with hydrated lime as an additive were lower than the viscosities of asphalts extracted from the same bituminous mixtures without hydrated lime.

VOLUME REDUCTION AND SOLIDIFICATION OF LOW-LEVEL RADIOACTIVE WASTES

Stewart, John E.
Werner & Pfleiderer
Power Eng (Barrington, IL) v 84, n 2, Feb 1980, p 64-65
CODEN: POENAI ISSN: 0032-5961

Recent restrictions at low-level radwaste burial sites and increased in costs have made it more important to reduce the volume of material shipped to the sites. In one process that has emerged from R&D work, the radwaste is dewatered and mixed with hot asphalt in an extruder-evaporator. The product is discharged into containers where it solidifies upon cooling. Asphalt has several characteristics which make it attractive for this process. It is thermoplastic, and solidification requires only the removal of the process heat; it resists leaching radiation and bacterial attack; it has good tolerance for oil and resists pH variations in the feed stream. It is low in cost; it is sample to handle and to store; and retrievability is practical.

VOLUME REDUCTION AND SOLIDIFICATION USING ASPHALT

Doyle, Richard D.; Stewart, John E.
Werner & Pfleiderer Corp., Waldwick, NJ
Waste Manage and Fuel Cycles '78; Proc of the Symp on Waste Manage, Tucson, AZ, Mar 6-8 1978, Publ by Ariz Board of Regents, Tucson, 1978, p 268-277.

Volume reduction of the radioactive waste produced is essential if the nuclear power industry is to grow and assume its natural place in the production of electricity past the year 1980. One of the prime concerns of all persons connected with the nuclear industry is where the waste produced will be permanently stored. The Volume Reduction and Solidification (VRS) system appears to be the only system available that provides both volume reduction and solidification in a binder that fully meets the IAEA criteria. This system uses a simple mechanical process that in one step removes all unwanted water from the waste, while homogenizing the remaining radioactive constituents with liquid asphalt for discharge into a container. Once this waste-asphalt mix has cooled, a significant volume reduction effect is realized in an end product that meets even the most stringent requirements. In addition to this, the system returns all water to the plant for reuse, thereby limiting the need for additional makeup. (14 refs.)

Descriptors: Industrial wastes, radioactive materials, asphalt, applications, nuclear reactors, spent fuels.

Classification Codes: 622, 621, 411

APPENDIX C

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APPENDIX D

GLOSSARY OF CEMENT CHEMISTRY TERMINOLOGY

There are a variety of terms and chemical formula notations. This section of the literature survey presents cement chemistry terms and definitions that are germane to this report and stabilization/solidification processes. All terms and definitions are taken from the ACI Manual of Concrete Practice - Part 1 (1980).

Cement chemists use a type of shorthand notation to designate compounds occurring in the production of concrete. Table D-1 lists the shorthand notations used in this report and recognized by the concrete industry.

TABLE D-1. CEMENT CHEMISTS' SHORTHAND NOTATION

Chemical compound	Shorthand notation
CaO	C
SiO_2	S
H_2O	H
Al_2O_3	A
Fe_2O_3	F
Na_2O_3	N
K_2O	K
SO_3	$\bar{S}$
Salicylic acid	SA
Calcium lignosulfonate	CLF
Sodium lignosulfonate	NLS
Hydrated calcium silicate gel	C-S-H
Tetracalcium-aluminoferrite (celite)	C_4AF
Tricalcium silicate (alite)	C_3S
Tricalcium aluminate	C_3A
beta-Dicalcium silicate (belite)	C_2S

Source: Popovics 1979.

Absorption: The process by which a liquid is drawn into and tends to fill permeable pores in a porous solid body; also, the increase in weight of a porous solid body resulting from the penetration of a liquid into its permeable pores.

Acceleration: Increase in velocity or in rate of change, especially the quickening of the natural progress of a process, such as hardening, setting, or strength development of concrete.

Accelerator: A substance which, when added to concrete, mortar, or grout, increases the rate of hydration of the hydraulic cement, shortens the time of setting, or increases the rate of hardening of strength development, or both.

Admixture: A material other than water, aggregates, and hydraulic cement, used as an ingredient of concrete or mortar, and added to the concrete immediately before or during its mixing.

Adsorbed water: Water held on surfaces of a material by electrochemical forces and having physical properties substantially different from those of absorbed water or chemically combined water at the same temperature and pressure.

Adsorption: Development at the surface of a liquid or solid of higher concentration of a substance than exists in the bulk of the medium; especially, formation of one or more layers of molecules of gases, of dissolved substances, or of liquids at the surface of a solid, such as cement, cement paste, or aggregate, or of air-entraining agents at the air-water interfaces; also, the process by which a substance is adsorbed.

Cement gel: The colloidal material that makes up the major portion of the porous mass of which mature hydrated cement paste is composed.

Cement, Portland: A hydraulic cement produced by pulverizing clinker consisting essentially of hydraulic calcium silicates, and usually containing one or more of the forms of calcium sulfate as an interground addition.

Cement, Portland blast-furnace slag: A hydraulic cement consisting essentially of an intimately interground mixture of Portland cement clinker and granulated blast-furnace slag or an intimate and uniform blend of Portland cement and fine granulated blast-furnace slag in which the amount of the slag constituent is within specified limits.

Cement, Portland-pozzolan: A hydraulic cement consisting essentially of an intimate and uniform blend of Portland cement or Portland blast-furnace slag cement and fine pozzolan produced by intergrinding Portland-cement clinker and pozzolan, by blending Portland cement or Portland blast-furnace slag cement and finely divided pozzolan, or a combination of intergrinding and blending, in which the pozzolan constituent is within specified limits.

Cementation process: The process of injecting cement grout under pressure into certain types of ground (e.g., gravel, fractured rock) to solidify it.

Clinker: A partially fused product of a kiln, which is ground to make cement; also other vitrified or burnt material.

Compressive strength: The measured maximum resistance of a concrete or mortar specimen to axial loading; expressed as force per unit cross-sectional area; or the specified resistance used in design calculations, in the U.S. customary units of measure expressed in pounds per square inch (psi) and designated fc' .

Concrete: A composite material that consists essentially of a binding medium within which are embedded particles or fragments of aggregate; in Portland cement concrete, the binder is a mixture of Portland cement and water.

Curing: Maintenance of humidity and temperature of freshly placed concrete during some definite period following placing, casting, or finishing to ensure satisfactory hydration of the cementitious materials and proper hardening of the concrete.

Damp-proofing: Treatment of concrete or mortar to retard the passage or absorption of water, or water vapor, either by application of a suitable coating to exposed surfaces, or by use of a suitable admixture or treated cement, or by use of preformed films such as polyethylene sheets under slabs on grade.

Entrained air: Microscopic air bubbles intentionally incorporated in mortar or concrete during mixing, usually by use of a surface-active agent; typically between 10 and 1000 µm in diameter and spherical or nearly so.

Entrapped air: Air voids in concrete which are not purposely entrained and which are significantly larger and less useful than those of entrained air, 1 mm or larger in size.

Ettringite: A mineral, high sulfate calcium sulfoaluminate ($3\ CaO \cdot Al2^{0}3 \cdot 3\ CaSO_4 \cdot 30\text{-}32\ H_2O$), also written as $Ca_6[Al(OH)_6]_2 \cdot 24\ H_2O\ [(SO_4)_3 \cdot 1\frac{1}{2}\ H_2O]$; occurring in nature or formed by sulfate attack on mortar and concrete; the product of the principal expansion-producing reaction in expansive cements; designated as "cement bacillus" in older literature.

False set: The rapid development of rigidity in a freshly mixed Portland cement paste, mortar, or concrete without the evolution of much heat, which rigidity can be dispelled and plasticity regained by further mixing without addition of water; premature stiffening, hesitation set, early stiffening, and rubber set are terms referring to the same phenomenon, but false set is the preferred designation.

Final set: A degree of stiffening of a mixture of cement and water greater than initial set, generally stated as an empirical value indicating the time in hours and minutes required for a cement paste to stiffen sufficiently to resist, to an established degree, the penetration of a weighted test needle; also applicable to concrete and mortar mixtures with use of suitable test procedures.

Flash set or quick set: The rapid development of rigidity in a freshly mixed Portland cement paste, mortar, or concrete, usually with the evolution of considerable heat, which rigidity cannot be dispelled nor can the plasticity be regained by further mixing without addition of water; also referred to as quick set or grab set. The important difference between false and given by definition and indicated by penetration results is the ability to dispel or not to dispel the set. If the set is dispelled by further mixing it is falso set: if not dispelled, it is quick set.

Grout: A mixture of cementitious material and water, with or without aggregate, proportioned to produce a pourable consistency without segregation of the constituents; also, a mixture of other composition but of similar consistency.

Normal set: The retention of plasticity by a cement paste during a period of time required for proper and easy placing, nominally in the order of 5 to 20 minutes. Such set would be reflected by full-depth penetration of the mortar, 50 mm, during the first 11 minutes or longer. Eventually, setting would occur with attendant gradual stiffening of the mortar and decreased needle penetration.

Plasticity: A complex property of a material involving a combination of qualities of mobility and magnitude of yield value; that property of freshly mixed cement paste concrete, or mortar which determines its resistance deformation or ease of molding.

Portland cement: see cement, Portland.

Pozzolan: A siliceous or siliceous and aluminous material, which in itself possesses little or no cementitious value but will, in finely divided form and in the presence of moisture, chemically react with calcium hydroxide at ordinary temperatures to form compounds possessing cementitious properties.

Retardation: Reduction in the rate of hardening or setting, i.e., increase in the time required to reach initial and final set or to develop early strength of fresh concrete, mortar, or grout.

Retarder: An admixture that delays the setting of cement paste, and hence of mixtures such as mortar or concrete containing cement.

Slump: A measure of consistency of freshly mixed concrete, mortar, or stucco equal to the subsidence measured to the nearest 1/4 in. (6 mm) of the molded specimen immediately after removal of the slump cone.

Slump cone: A mold in the form of the lateral surface of the frustum of a cone with a base diameter of 8 in. (203 mm), top diameter 4 in. (102 mm), and height 12 in. (305 mm), used to fabricate a specimen of freshly mixed concrete for the slump test; a cone 6 in. (152 mm) high is used for tests of freshly mixed mortar and stucco.

Slump loss: The amount by which the slump of freshly mixed concrete changes during a period of time after an initial slump test was made on a sample or samples thereof.

Spall: A fragment, usually in the shape of a flake, detached from a large mass by a blow, by the action of weather, by pressure, or by expansion within the larger mass; a small spall involves a roughly circular depression not greater than 20 mm in depth nor 150 mm in any dimension; a large spall may be roughly circular or oval or, in some cases, elongated, more than 20 mm in depth, and 150 mm in greatest dimension.

Thixotropy: The property of a material that enables it to stiffen in a short period on standing, but to acquire a lower viscosity on mechanical agitation, the process being reversible; a material having this property is termed thixotropic or shear thinning.

Water-reducing agent: A material that either increases slump of freshly mixed mortar or concrete without increasing water content or maintains workability with a reduced amount of water, the effect being due to factors other than air entrainment.